

Paul R. Robinson

Introduction

Petroleum makes the world go around. In the realm of global economics and politics, that statement is hard to dispute. Petroleum is uniquely versatile. When wisely handled, it is safe and clean. It is still abundant, and it can be stored for years at a time simply by leaving it in the ground. Under ambient conditions, it is a liquid and relatively noncompressible, so it can be carried across oceans in large tankers or pumped through pipelines hundreds of miles long. Its distilled products have high energy densities. Fifteen gallons of gasoline can move a 3,300-lb automobile across 350 flat miles at 65 miles per hour. (In metric units, those values are 57 L, 1,480 kg, 565 km, and 105 kph.) We transform petroleum into thousands of useful substances: fuels, lubricants, and chemicals with exceedingly different properties—from baby oil to pesticides, from adhesives to laxatives, from artificial sweeteners to sulfuric acid (Tables 18.1 and 18.2).

Crude oil and its coproduced cousin, natural gas, provide nearly 60 % of our energy (Fig. 18.1). Petroleum makes poor countries rich, and the economic health of rich countries depends on its cost and availability. Petroleum and its derivatives—especially fuels and explosives—have played a major role in all major wars since the start of the twentieth Century. And lest we forget: our unabating dependence on petroleum, natural gas, and other fossil hydrocarbons impacts the quality of our air, our water, and the earth itself.

Economics and politics. One cannot overstate the impact of petroleum on world economics and politics. The supply/demand picture is heavily skewed. As shown in Table 18.3, in 2008 the Middle East consumed far less oil than it produced, accounting for 7.7 % of global consumption but 30 % of global production; the 7.7 % is misleadingly high,

because it includes the energy consumed to convert crude oil into exported products. Conversely, the United States and Western Europe consumed far more than they produced. The United States holds only 1.6 % of proven reserves, but it was the third largest producer (10.0 %) and by far the largest consumer (22.8 %). From January 2010 through March 2011, petroleum-related imports were responsible for 34–50 % of the total US trade deficit (Fig. 18.2).

Due to the need to import so much of such a valuable commodity—much of which is obtained from hostile and/or sensitive environs such as the North Sea, the North Slope of Alaska, and offshore California—the world's largest economies are vulnerable. Politics can be hostile, too. The Arab Oil Embargos of 1967 and 1973–1974 and the Iranian Revolution of 1979 caused prices to increase dramatically. The events correspond to price spikes in Fig. 18.3, which shows how petroleum prices have varied since 1861. Figure 18.3 also shows that prices in 2010 were at historical highs, both in present-day and inflation-corrected dollars. Both in the 1970s and recently, the higher prices led to reduced consumption (Fig. 18.4).

Consumption began to fall immediately, but it took a few years to reach “bottom.” People started buying smaller cars, but not all at once. And while it's easy for people to drive less and install low-wattage light bulbs, it takes time to replace old equipment with newer, more-efficient equipment in power plants and factories. Unfortunately, the consumption “bottom” was transitory. When prices fell, consumption went back up.

Data selected from [3] show that 2009 was a year of milestones for the following reasons:

1. Global primary energy consumption fell by 1.1 %, the largest decline since 1980
2. OPEC oil production fell by 7.3 %, the largest decline since 1983
3. Natural gas production fell by 2.1 %, the first decline on record
4. Coal's share of world energy consumption rose to 29.4 %, the highest since 1970

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Table 18.1 Selected petroleum products

Product	Uses, comments
Fuels	
Propane	Home heating, motor vehicles
n-Butane	Gasoline blend stock, portable lighters
i-Butane	Gasoline blend stock, production of C7 alkylate for gasoline
Naphtah/gasoline	Spark-ignition engine fuel. Several different grades
Kerosene/jet	Home heating, illumination. Airplane fuel. Several grades
Gas oil/diesel	Diesel fuel. Four major grades including ULSD ^a
Fuel oil	Six major grades
Petroleum coke	Power plant fuel, fuel, and anodes for making steel
Lubricants	
>> 800 products—from “baby oil” to axle grease—all with stringent specifications	
Construction materials	
Asphalt	Paved roads, water-proofed buildings. Four major classes
Waxes	Coated paper packaging, water-proofing, candles
Miscellaneous	
Sulfur	Sulfuric acid and fertilizers
Needle coke	Anodes for making aluminum and high-grade steel
Graphite	Metallurgy, specialty fibers, paints, pencils

^aULSD stands for ultra-low-sulfur diesel

5. China and the United States accounted for similar percentages of total world energy consumption. Per Table 18.4: in 2009 China consumed 0.2% less than the United States—2,177 MTOE vs. 2,182 MTOE, respectively, where MTOE stands for million tonnes of oil equivalent. On a per capita basis, US consumption was 4.2 times higher than China's.

The first four milestones can be attributed to the record-high cost of oil and gas. As mentioned, people can and do conserve when energy prices go high enough.

Insert: primary energy sources vs. energy vectors. Periodically, news reporters tout zero-emission electric cars or hydrogen-powered vehicles that produce nothing but water. But when one considers the ultimate source of the electricity and hydrogen, such vehicles can be very dirty indeed.

Electricity is not a primary source of energy. It is an energy vector, generated from primary sources and carried through power lines to energy consumers.

Molecular hydrogen also can serve as an energy vector. (In the Sun, of course, where hydrogen undergoes nuclear fusion, it is a primary energy source.) On Earth, commercial hydrogen production plants employ the steam reforming of hydrocarbons or the electrolysis of water. Steam reforming coproduces CO₂, a significant “green-house gas.” Electrolysis also produces CO₂ if the required electricity comes from

Table 18.2 Selected petrochemicals and uses

Petrochemicals	Used to make
Alcohols	
Methanol	MTBE, acetic acid, formaldehyde . . .
Acetic acid	Vinyl acetate ⇒ plastics, latex paints. Cellulose acetate
Cellulose acetate	Yarns, sheet plastic, films, lacquers
Formaldehyde	Resins, butanediol, inks, nylon
Ethyl alcohol	Gasoline, solvents, personal care products, ethyl chloride, ethyl acetate . . .
Ethyl acetate	Solvent (e.g., nail polish remover)
Isopropyl alcohol	Solvents, personal care products
Higher alcohols	Solvents, plasticizers, detergents
Aromatics	
Benzene	Styrene, cumene, cyclohexane, maleic anhydride . . .
Toluene	Polyurethane, gasoline
Xylenes	Polyester fibers, resins, plasticizers, gasoline
Aromatics derivatives	
Cyclohexane	Nylon precursors
Cumene and phenol	Phenolic resins, epoxy, and polycarbonate resins
Olefins	
Ethylene	Polyethylene, ethylene dichloride, ethylene oxide
Ethylene dichloride	Polyvinyl chloride (PVC) ⇒ plastics
Ethylene oxide	Polystyrene, ethylene glycol
Ethylene glycol	Antifreeze, polyethylene terephthalate (PET) ⇒ plastic bottles
Propylene	Polypropylene, propylene oxide ⇒ propylene glycol
Propylene glycol	Antifreeze, polyesters, pharmaceuticals, hand sanitizers
Butenes	Maleic anhydride . . .
Butadiene	Complex polymers, including synthetic rubbers
Alpha olefins	Polymers, surfactants, synthetic lube oil and additives, fatty acids
Other	
Acrylonitrile, acrylic acid	Polymers, including transparent polymers (Plexiglass, Lucite)
Aldehydes and ketones	Acetic acid, acetone, other solvents
Isobutane	Methylmethacrylate resins
Maleic anhydride	Polyesters, resins, plasticizers, dicarboxylic acids, Nylon precursors

coal, oil, or natural gas. Thanks to environmental laws, burning fossil fuels is cleaner than it used to be, but it still generates CO₂, sulfur compounds, nitrogen compounds, and in the case of coal, significant amounts of ash. If the electricity comes from hydroelectric or nuclear power plants, then electrolytic hydrogen is carbon-neutral. Compared to electricity, hydrogen is easier to store. As hydrogen gas, it is kept in salt domes, high-pressure tanks, and caverns such the ones near Borger and Sweeney, Texas. It is also stored as a hydride in special metal alloys. Hydrogen is transported from production plants or storage facilities through pipelines or in tube trailers.

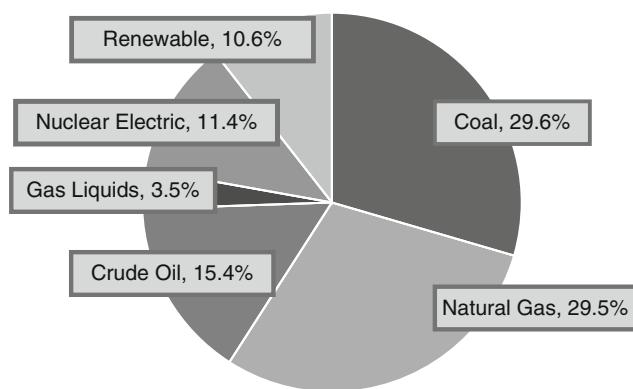


Fig. 18.1 Worldwide primary production of energy, 2007. Based on data from the U.S. Energy Information Administration (EIA) [1, 2]

Insert: conservation and production efficiency. When discussing the future of energy supply and demand, it is important to consider the potential for increased conservation and power production efficiency.

According to a report by the Rocky Mountain Institute [4], energy production efficiency in the United States increased 65–75 % since 1970. The ten top-performing states accounted for a large portion of the increase, creating a huge efficiency gap between the top-performing states and the rest of the nation; the data were normalized for differences in climate and the ratio of residential vs. industrial consumption. If the rest of the country achieved the same electric productivity as the Top Ten, the country would save about 1.2 million gigawatt-hours annually. This is equivalent to 30 % of the nation's total power consumption and 62 % of its coal-based power. The return on investment for efficiency improvement depends on several factors, especially economy of scale and the cost of capital, but the top-performing states achieved significant returns when interest rates were 3–5 times higher than in 2011. Power production from fossil fuels is responsible for 39 % of all CO₂ emissions in the United States, so a 30 % improvement in power production efficiency would lead to a huge reduction in CO₂ production [5].

Table 18.3 Worldwide petroleum reserves, production, and consumption in 2008

	Oil reserves		Oil production		Oil consumption	
	10 ⁹ Barrels	Percent (%)	Percent MBPD	Percent (%)	Percent MBPD	Percent (%)
North America	212	15.9	15,032	17.6	23,896	28.0
Canada	179	13.4	3,332	3.9	2,260	2.6
Mexico	12	0.9	3,187	3.7	2,128	2.5
United States	21	1.6	8,514	10.0	19,498	22.8
Central, S. America	110	8.2	7,411	8.7	6,167	7.2
Brazil	12	0.9	2,439	2.9	2,520	2.9
Venezuela	87	6.5	2,639	3.1	760	0.9
Europe	14	1.1	5,218	6.1	16,145	18.9
France	0.1	0.0	80	0.1	1,986	2.3
Germany	0.4	0.0	151	0.2	2,569	3.0
Italy	0.4	0.0	164	0.2	1,639	1.9
Norway	6.9	0.5	2,464	2.9	220	0.3
United Kingdom	3.6	7.4	12,535	14.7	4,333	5.1
Eurasia	99	7.4	12,535	14.7	4,333	5.1
Kazakhstan	30	2.3	1,431	1.7	239	0.3
Russia	60	4.5	9,794	11.5	2,900	3.4
Middle East	748	56.2	25,841	30.2	6,568	7.7
Iran	138	10.4	4,180	4.9	1,755	2.1
Iraq	115	8.6	2,386	2.8	638	0.7
Kuwait	104	7.8	2,729	3.2	325	0.4
Qatar	15	1.1	1,203	1.4	129	0.2
Saudi Arabia	267	20.0	10,783	12.6	2,297	2.7
United Arab Emirates	98	7.3	3,046	3.6	463	0.5
Africa	115	8.6	10,879	12.7	3,216	3.8
Algeria	12	0.9	2,181	2.6	299	0.3
Angola	9.0	0.7	2,014	2.4	64	0.1
Libya	41	3.1	1,875	2.2	273	0.3
Nigeria	36	2.7	2,169	2.5	286	0.3
Asia & Oceania	34	2.6	8,592	10.0	25,138	29.4
China	16	1.2	3,987	4.7	7,850	9.2
India	5.6	0.4	888	1.0	2,940	3.4
Japan	0.0	0.0	134	0.2	4,785	5.6
World	1,332	100	85,507	100	85,462	100

Based on data [1]

and because we use similar technology to discover and recover them.

Fossil Hydrocarbons: Categories

Industry professionals divide fossil hydrocarbons into several categories. As with many things in the oil industry, the definitions are functional and the distinctions can be fuzzy, especially between heavy oil and bitumen. Natural gas is often lumped with liquid petroleum in articles such as this, because underground oil is always associated with gas,

Gases

Natural gas is fully discussed in Chap. 20. Here, it is sufficient to say the following:

- Natural gas contains mostly methane (CH₄)
- So-called *wet gas* contains significant amounts of butanes, pentanes, and heavier hydrocarbons, which can

Fig. 18.2 United States total trade deficit and the trade deficit due to petroleum. Based on data from the U.S. Energy Information Administration [1]

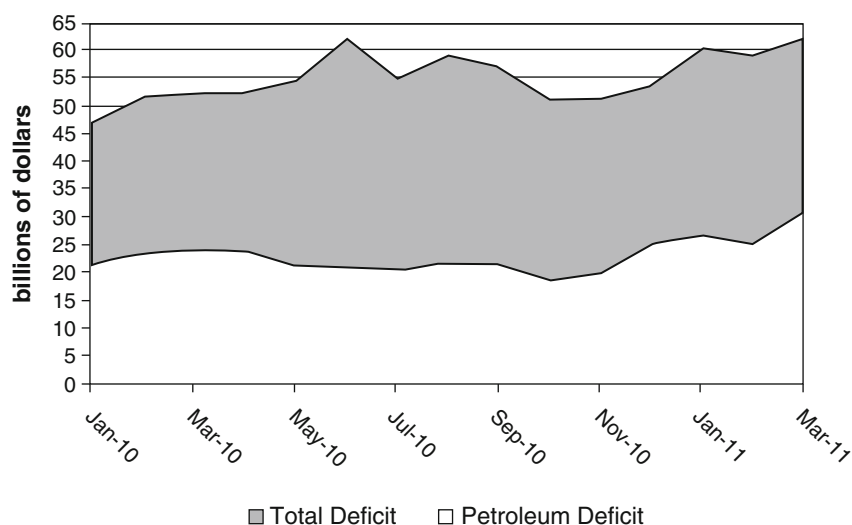
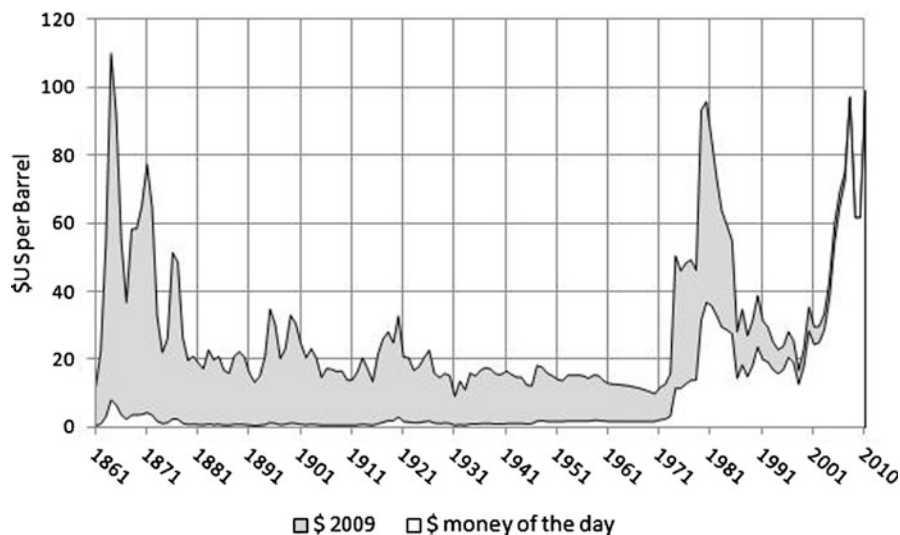


Fig. 18.3 Cost of petroleum since 1861. Based on data from [3]



be recovered as liquid condensate in natural gas processing plants

- *Dry gas* includes only traces of higher hydrocarbons
- *Sour gas* contains hydrogen sulfide, and *acid gas* contains carbon dioxide and/or hydrogen sulfide. Sour-gas processing plants coproduce elemental sulfur, which is used to make sulfuric acid and fertilizers

Some natural gas contains commercial quantities of inert gases—helium, neon, and/or argon. Almost all commercial helium comes from natural gas plants [6].

Liquids

Crude oil is the common name for liquid petroleum. People refer to crude oil as a single substance, but there are hundreds of different crudes with significantly different

compositions. Crudes typically are named for their source country, reservoir, and/or some distinguishing physical or chemical property. Table 18.5 presents selected physical and chemical properties for ten crude oils.

In sweet crudes such as Tapis, the sulfur content is low. Sour crudes have more sulfur, which gives them a tart taste. (That's right: In the old days, prospectors did indeed characterize crude oil by tasting it.) Synthetic crude oil is produced from coal, kerogen, or natural bitumen. Processing costs are higher for conventional or synthetic crudes with high density and large amounts of sulfur, nitrogen, and trace contaminants. *Heavy oil* has a density greater than 1.0, so it sinks in water. The viscosities of heavy oil range from about 5,000 to 10,000 cP.

For the examples in Table 18.5, the sulfur content ranges from 0.14 wt.% to 5.3 wt.%, and the nitrogen content ranges from nil to 0.81 wt.%. The density (specific gravity) ranges from 0.798 to 1.014.

Fig. 18.4 Petroleum consumption since 1970 [3]

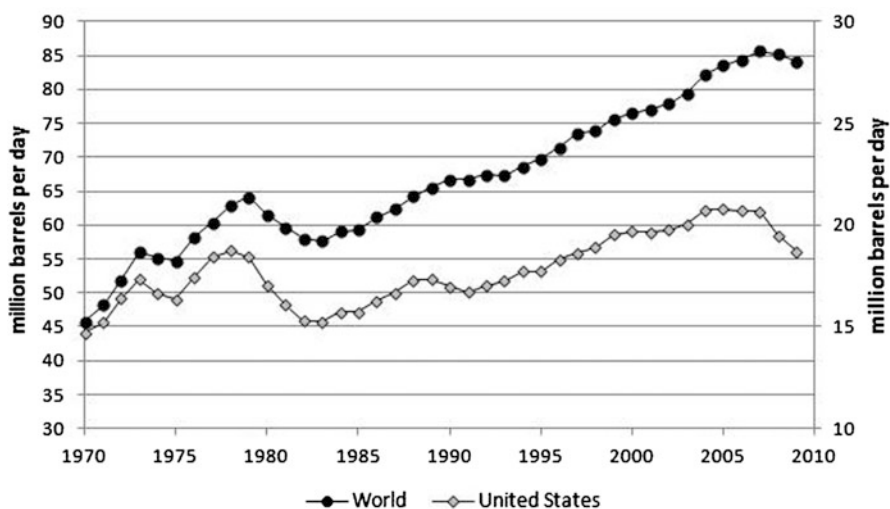


Table 18.4 Global changes by region in total energy consumption: 2009 vs. 2008

Region/country	Change 2009 vs. 2008 (%)	2009 Share of world total (%)
Total North America	−4.7	23.9
United States	−5.0	19.5
Total Europe/Eurasia	−6.0	24.8
Russian Federation	−6.4	5.7
Total Africa	−1.1	3.2
Total Asia Pacific	4.4	37.1
Japan	−8.0	4.2
China	8.7	19.5
India	6.6	4.2

Data selected from [3]

A commercial crude oil assay determines the chemical and physical properties of the whole crude and several distilled fractions. The fractions correspond to boiling ranges for common fuels. Using assay reports, refiners and oil traders determine the value of a crude by comparing its properties with refinery specifications, which include distillate properties and limits on trace contaminants. Limits on sulfur content can be set by sulfur-plant constraints or by the metallurgy of process equipment. Other common constraints include TAN (total acid number) and trace-metal content. Traders do purchase off-spec crudes, but usually for subsequent trading.

Table 18.6 shows an abbreviated template for a detailed assay report. Table 18.7 shows distillation yields for four common crudes. The naphtha content of Brent is twice as high as Ratawi, and its vacuum residue content is 60 % lower. Bonny Light yields the most middle distillate and the least amount of vacuum residue.

Table 18.5 Selected properties of ten crude oils [7]

Crude oil	API gravity ^a	Residue ^b (vol%)	Sulphur (wt%)	Nitrogen (wt%)
Alaska North Slope	27.1	53.7	1.2	0.2
Arabian Light	33.8	54.2	1.8	0.07
Arabian Heavy	28.0	46.6	2.8	0.15
Athabasca	8	50.8 ^c	4.8	0.4
Brent (North Sea)	39	38.9	0.3	0.10
Boscan (Venezuela)	10.2	82.8	5.5	0.65
Kuwait export	31.4	49.5	2.6	0.21
Shengli (China)	24.7	72.5	1.0	
Tapis blend (Malaysia)	45.9	26.3	0.028	0.018
West Texas	40.2	36.4	0.3	0.08

^aAPI Gravity is related to specific gravity by the formula: $API = 141.5 \div (\text{specific gravity @ } 60^\circ\text{F}) - 131.5$

^bUnless otherwise stated, cut point = 343 °C–plus (650 °F–plus)

^cCutpoint = 525 °C (913 °F)

Bitumen

Like heavy oils, natural bitumens have densities greater than 1.0, but the viscosities are higher—more than >10,000 cP. Under ambient conditions, natural bitumen is a tar or a solid, but when heated it softens and flows. In practical terms, it is recovered as a solid but transported and processed as a liquid.

(It is important at this point to distinguish between natural bitumen and refined bitumens. The latter are specialty products with rather tight specifications. Refined bitumens are used primarily for paving and construction.)

Natural bitumen was probably the first form of petroleum used by man. In 3000 BCE, Mesopotamians were lining water canals, sealing boats, and building roads with natural

Table 18.6 Template for a detailed crude oil assay report

	Whole crude	Light naphtha	Medium naphtha	Heavy naphtha	Kero	AGO	LVGO	HVGO	VR	AR
True boiling point, °C	Initial	10	80	150	200	260	340	450	570	340
True boiling point, °C	Final	80	150	200	260	340	450	570	End	End
True boiling point, °F	Initial	55	175	300	400	500	650	850	1,050	650
True boiling point, °F	Final	175	300	400	500	650	850	1,050		
Yield of cut (wt% of Crude)		×	×	×	×	×	×	×	×	×
Yield of cut (vol% of crude)		×	×	×	×	×	×	×	×	×
Gravity, API	×	×	×	×	×	×	×	×	×	×
Specific gravity	×	×	×	×	×	×	×	×	×	×
Sulfur, wt%	×	×	×	×	×	×	×	×	×	×
Nitrogen, ppm	×		×	×	×	×	×	×	×	×
Viscosity @ 50 °C (122 °F), cST	×			×	×	×	×	×	×	×
Viscosity @ 135 °C (275 °F), cST	×			×	×	×	×	×	×	×
Freeze point, °C				×	×	×	×			
Freeze point, °F				×	×	×	×			
Pour point, °C	×			×	×	×	×	×	×	×
Pour point, °F	×			×	×	×	×	×	×	×
Smoke point, mm				×	×	×				
Aniline point, °C			×	×	×	×	×	×		
Aniline point, °F			×	×	×	×	×	×		
Cetane index, ASTM D976				×	×	×				
Diesel index			×	×	×	×	×	×		
Characterization factor (K)	×	×	×	×	×	×	×	×	×	×
Research octane number, Clear		×	×	×						
Motor octane number, Clear		×	×							
Paraffins, vol%		×	×	×	×	×	×			
Naphthenes, vol%		×	×	×	×	×	×	×		
Aromatics, vol%		×	×	×	×	×	×	×		
Heptane Asphaltenes, wt%	×								×	×
Micro carbon residue, wt%	×								×	×
Rams bottom carbon, wt%	×								×	×
Vanadium, ppm	×								×	×
Nickel, ppm	×								×	×
Iron, ppm	×								×	×

Table 18.7 Distillation yields for four selected crude oils [7]

Source field	Brent	Bonny Light	Green Canyon	Ratawi
Country	Norway	Nigeria	USA	Mid East
API gravity	38.3	35.4	30.1	24.6
Specific gravity	0.8333	0.8478	0.8752	0.9065
Sulfur, wt%	0.37	0.14	2.00	3.90
Yields, wt% feed				
Light ends	2.3	1.5	1.5	1.1
Light naphtha	6.3	3.9	2.8	2.8
Medium naphtha	14.4	14.4	8.5	8.0
Heavy naphtha	9.4	9.4	5.6	5.0
Kerosene	9.9	12.5	8.5	7.4
Atmospheric gas oil	15.1	21.6	14.1	10.6
Light VGO	17.6	20.7	18.3	17.2
Heavy VGO	12.7	10.5	14.6	15.0
Vacuum residue	12.3	5.5	26.1	32.9
Total naphtha	30.1	27.7	16.9	15.8
Total middle distillate	25.0	34.1	22.6	18.0
Naphtha plus distillate	55.1	61.8	39.5	33.8

bitumen. Egyptians were greasing chariot wheels with pitch and embalming mummies with asphalt [8, p. 2].

In tar sands, bitumen is associated with sand and clay, from which it can be recovered with hot water or steam. Tar sands (also known as oil sands) contain much of the world's recoverable oil. The largest deposits are in Alberta, Canada, where the proven reserves are 170 billion barrels; in addition, the province holds 1.4 billion barrels of conventional crude [9]. In the United States, tar sands are found primarily in Eastern Utah, mostly on public lands. These deposits contain 12–19 billion barrels of recoverable oil. In 2008, proven oil reserves in Venezuela totaled 87 billion barrels, mostly bitumen. In comparison, for that same year, Saudi Arabian reserves of conventional crude oil were 267 billion barrels [10].

Solids

Compared to liquids and gases, solids are harder to recover, transport, and refine. Liquids and gases can be pumped

Table 18.8 Typical composition of Green River oil shale [12]

Kerogen content: 15 wt.% ^a	
Kerogen composition, wt% of kerogen	
Carbon	80.5
Hydrogen	10.3
Nitrogen	2.4
Sulfur	1
Oxygen	5.8
Total	100
Minerals, wt% of mineral content	
Carbonates	48
Feldspars	21
Quartz	15
Clays	13
Analcite and pyrite	3
Total	100

^aEquivalent to 25 gal oil per ton of rock

through pipelines and into refineries with relative ease. Slurries of coal and water can be transported as liquids, but the water must be removed and eventually purified at considerable expense before the coal can be burned or gasified. Solid coal is consumed on a large scale to produce heat, steam, and electricity. These days, coal-powered transportation vehicles are rare. Coal-burning steam ships and railway locomotives are less efficient than their oil-powered counterparts. Typically, the specific energy of petroleum is 90 % greater than a ton of bituminous coal and 40 % greater than a ton of anthracite [11]. Even if for some reason a railroad or shipping company wanted to burn coal, doing so wouldn't be practical due to the present lack of coaling stations.

Kerogen is the solid organic matter in sedimentary rocks. Unlike bitumen, it doesn't flow even when heated. But at high-enough temperatures—e.g., 900 °F (480 °C)—it decomposes into gases, liquids, bitumen, and refractory coke. Huge amounts of kerogen are trapped in oil shale deposits. Fenton et al. [12] estimated that 1.3 trillion barrels of shale oil could be recovered from the world's oil shale reserves. Table 18.8 presents composition information on Green River oil shale from the western United States. About 91 % of the kerogen is hydrogen and carbon, but only 15 % of the sample is kerogen. Shale oil—synthetic crude from oil shale—tends to contain high amounts of arsenic, a severe poison for refinery catalysts. Usually, the arsenic is removed in existing hydrotreating units with special high-nickel chemisorption catalysts, which trap the arsenic by forming nickel arsenides.

Coal and coal technology are fully discussed in Chap. 19. Here we just say that coal is a black or brown combustible rock composed mostly of carbon, hydrocarbons, and ash. Generally, it is classified into four ranks—anthracite, bituminous, sub-bituminous, and lignite. Anthracite contains 86–97 % carbon and has a high heating value. Anthracite is relatively rare. Bituminous coal is far more common. It

Table 18.9 US consumption of petroleum products: average for 1991–2011.

Product	Consumption (barrels/day)	Percent of total (%)
Gasoline	8,032	43.6
Jet fuel	1,576	8.6
Other middle distillates	3,440	18.7
Residual fuel oil	867	4.8
Other oils	4,501	24.4
Total consumption	18,416	100
Gasoline + jet + other middle distillates	13,048	70.8

Averages are based on data taken from [1]

contains 45–86 % carbon and is burned to generate electricity. It is also used extensively in the steel and iron industries. Sub-bituminous coal contains 35–45 % carbon, and lignite contains 25–35 % carbon. Lignite is crumbly, has a high moisture content and a relatively low heating value.

Over the years, special circumstances have driven the large-scale conversion of coal into liquids, both directly and indirectly. Direct processes convert coal into various combinations of coal tar, oil, water vapor, gases, and char. The coal tar and oil can be refined into high-quality liquid fuels. Slurry-phase hydrocracking technology achieves very high direct conversion of coal into liquids. Several coal conversion processes are described in a recent book by Speight [13].

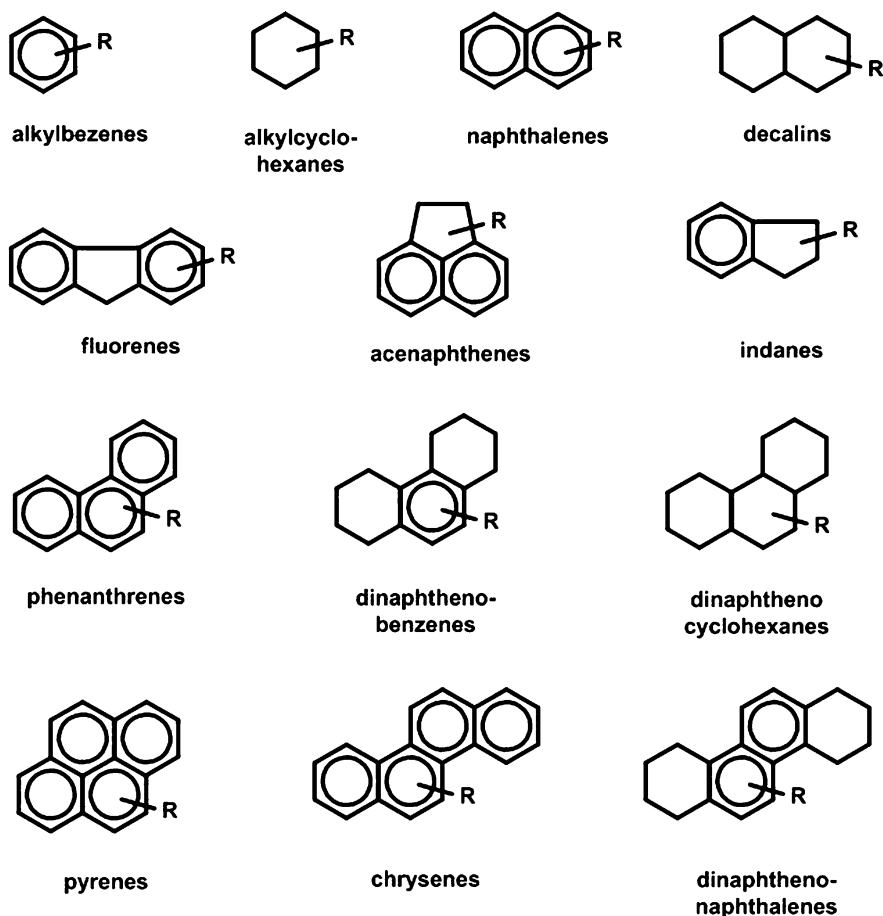
Developed in 1925, the Fischer-Tropsch (F-T) process is the main indirect route for converting coal into liquids. The coal is first gasified to make synthesis gas—a balanced mixture of CO and hydrogen. Over F-T catalysts, synthesis gas is converted into a full range of hydrocarbon products, including paraffins, alcohols, naphtha, gas oils, and synthetic crude oil. The F-T process was used extensively in Germany between 1934 and 1945. In South Africa, an improved version of the F-T process is used on a large scale to manufacture chemicals and fuels.

Synthesis gas is also derived from natural gas via steam-methane reforming. It can be converted into hydrogen and petrochemicals such as methanol. Worldwide, vast amounts of hydrogen are used to produce ammonia via the Haber-Bosch process.

Chemical Composition

The chemistry of the hydrocarbons in petroleum, bitumen, and kerogen is exceedingly complex. To one extent or another, they all contain water, inorganic salts, and dirt. After these are removed, most of the remaining compounds are hydrocarbons, some of which contain hetero atoms such

Fig. 18.5 Examples of hydrocarbon ring compounds



as sulfur, oxygen, and nitrogen, and trace metals. The non-hydrocarbon compounds can include different types of elemental sulfur. More than any other element, carbon binds to itself to form straight chains, branched chains, rings, and complex three-dimensional structures. The most complex molecules are biological—proteins, carbohydrates, fats, and nucleic acids. This is significant here because petroleum was formed from the remains of ancient microorganisms—primarily plankton and algae.

Figures 18.5, 18.6, and 18.7 show the complexity of petroleum. In addition to normal and isoparaffins (alkanes), it contains a large number of mono- and poly-ring hydrocarbons, to which paraffin chains can be attached (Fig. 18.5). Many compounds contain hetero atoms, especially sulfur, nitrogen, and/or oxygen (Fig. 18.6). Sulfur compounds also include aliphatic sulfides and disulfides.

Figure 18.7 shows plots of carbon number vs. atmospheric equivalent boiling point (AEBP) for different classes of compounds—aromatics, polynaphthenes, disulfides, benzothiophenes, etc. The indicated boiling points are for pure compounds. In mixtures, the boiling points are shifted by molecular interactions. Molecular interactions are greatest for polar compounds, such as those with hetero atoms. According to the Continuity Principle, physical and

chemical properties for a given class of compound vary continuously with the number of carbon atoms in attached alkyl groups. Boiling points are crucial, because fractional distillation is the primary means by which petroleum is separated into useful products. Boiling ranges for typical cuts—naphtha, kerosene (including jet fuel), AGO (atmospheric gas oil, including diesel fuel), vacuum gas oils, and residue—appear at the top Fig. 18.7. In practice, due to imperfect separation in commercial distillation towers, the fractions overlap.

Curve A is for normal paraffins. Branched isomers with the same carbon number boil at lower temperatures. Fully saturated poly ring compounds fall on *Curve B*. Fully unsaturated poly aromatics fall on *Curve C*. Phenanthrene ($C_{14}H_{10}$), a three-ring poly aromatic compound, is found in the AGO boiling range. Adding seven hydrogen molecules (14 hydrogen atoms) converts phenanthrene into perhydrophenanthrene ($C_{14}H_{24}$), which ends up in the kerosene cut. *Curve D* shows how adding alkyl groups to pyrene makes *Curve D* parallel to *Curve A*. *Curves E, F, and G* represent compounds containing hetero atoms—sulfur, nitrogen, and oxygen.

Figure 18.8 also illustrates the Continuity Principle, in this case with a plot of density versus molecular weight for

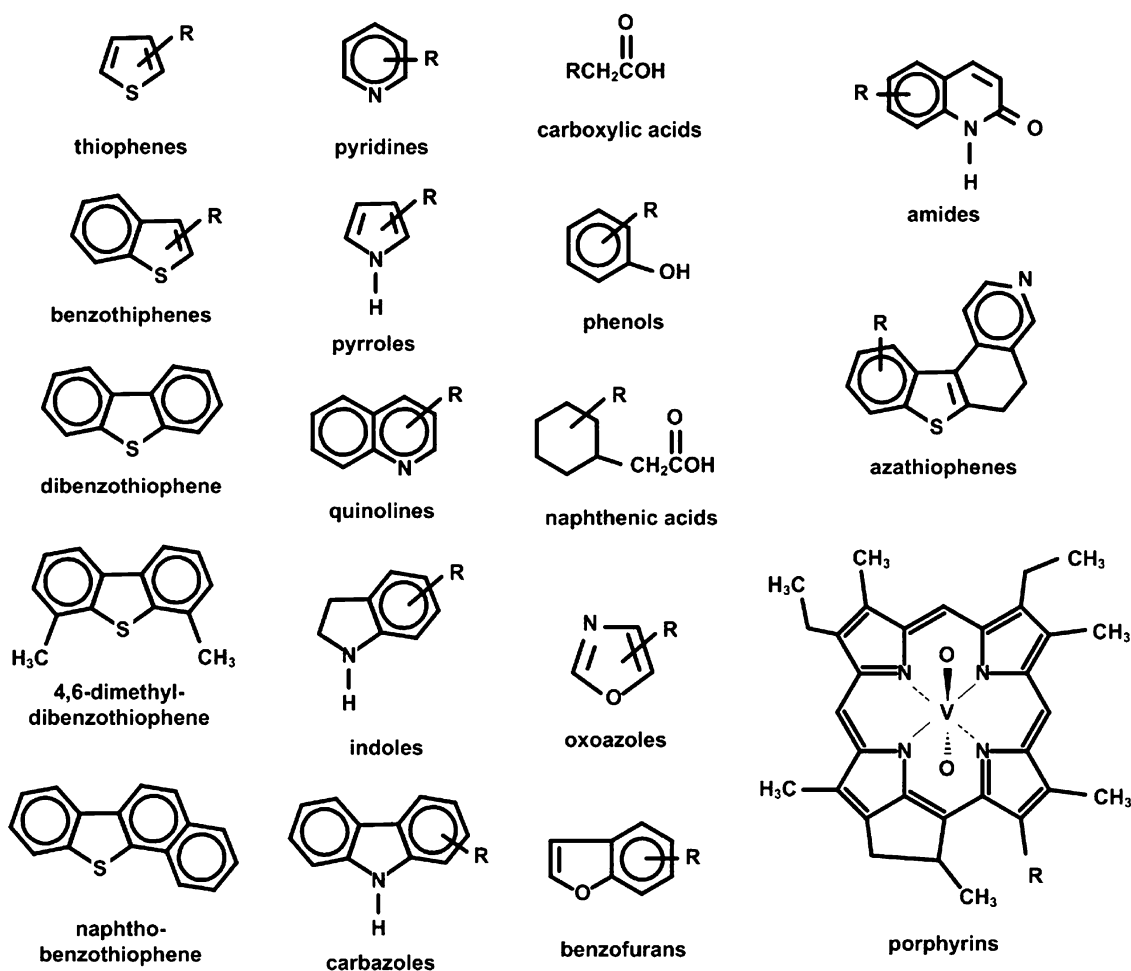


Fig. 18.6 Examples of hetero-atom compounds

five families of hydrocarbons. The “Z” number indicates hydrogen deficiency vs. paraffins. It comes from the subscript for hydrogen in the chemical formula C_nH_{2n+z} . For paraffins such as methane (CH_4) and octane (C_8H_{18}), $z = +2$, and the general formula is C_nH_{2n+2} . For benzene (C_6H_6) and alkylbenzenes, $z = -6$, and the general formula is C_nH_{n-6} .

Origin

Petroleum is complex due to its origin. According to Walters [17], eighteenth Century scientists concluded that coals were derived from plant remains. Mikhailo Lomonosov gets credit for suggesting that petroleum and bitumen were produced underground from coal at high pressure and temperature. In the mid-nineteenth Century, T.S. Hunt concluded that the organic matter in certain rocks comes from marine plants or animals.

Modern scientists believe petroleum came primarily from plankton and algae in the following way: the remains of dead

organisms accumulated at the bottoms of ancient lakes or seas, along with sand, clay, salts, and other material. Over time, pressure, and heat transformed the deposits into sedimentary rock. Depending on the origin of the organic matter and the environment in which it aged, it became coal, kerosene, bitumen, petroleum, or natural gas.

Biomarkers. In 1936, Alfred Treibs linked the chlorophyll in plants to the porphyrins in petroleum (Fig. 18.9). Even after millions of years, porphyrins and other biomarkers retain much of their original structure. Biomarkers can be found in crude oil, rocks, sediments, and soil extracts.

Exploration

A book by Conaway [18] presents a good overview of how we look for and produce petroleum. Commercially significant petroleum systems include the following:

- Organic-rich source rock in which oil and gas were formed

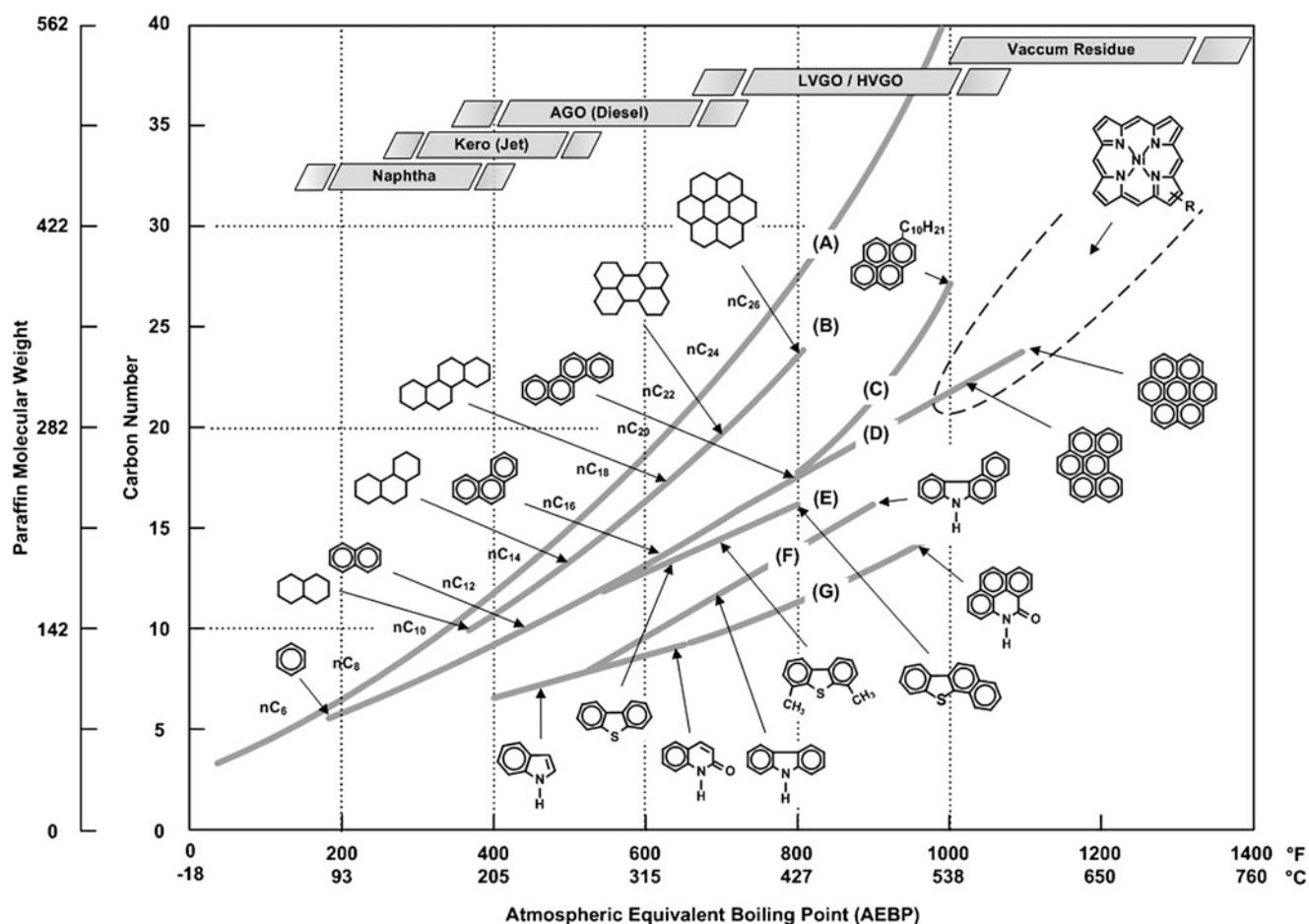


Fig. 18.7 Carbon number and atmospheric equivalent boiling points for different compounds [14, 15]. Shown at the top of the figure are the straight-run products that correspond to AEBPs of the compounds.

Note how the saturation of polyaromatics such as chrysene (4 rings), phenanthrene (3 rings), and naphthalene (2 rings) can move them into different distillation fractions

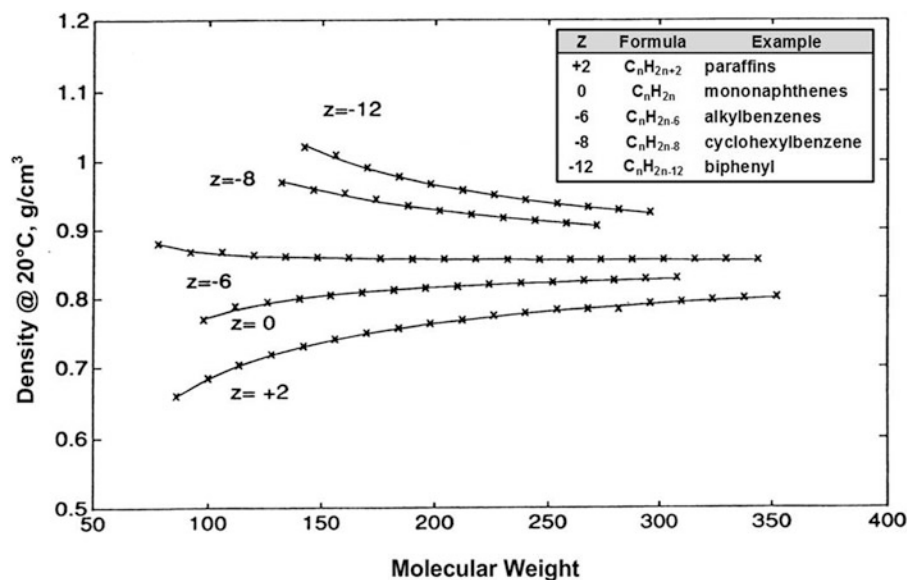
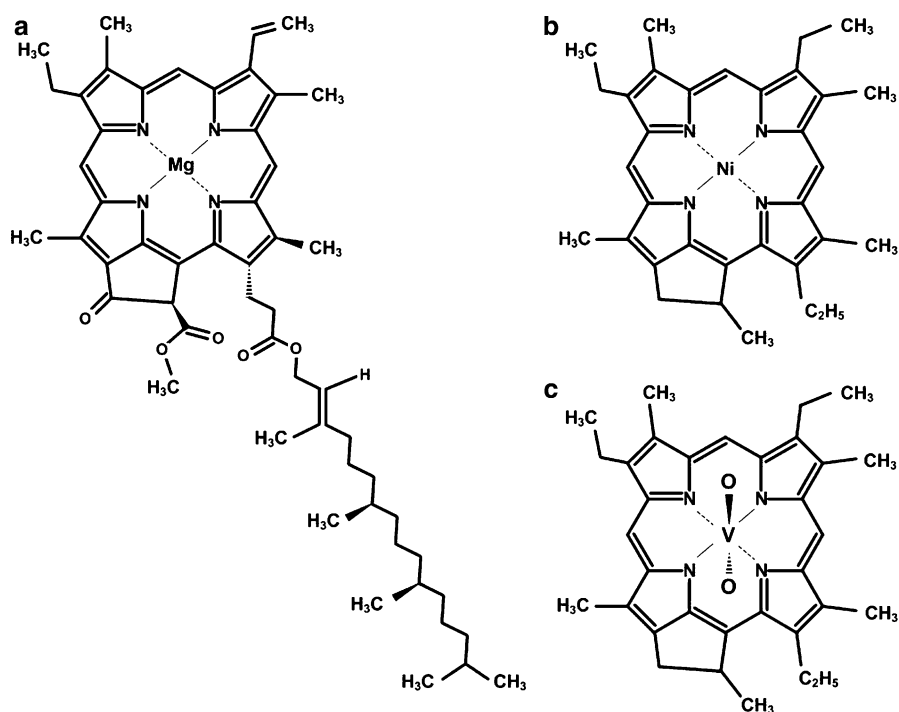


Fig. 18.8 Density vs. molecular weight for hydrocarbon families [16]

Fig. 18.9 Biomarkers: a comparison of Chlorophyll A with porphyrins found in petroleum



- Pathways comprised of permeable rock such as sandstone and limestone, which allow oil and gas to migrate. Often, the movement of oil and gas is promoted by the flow of underground water
- Porous, permeable reservoir rock capped by impermeable rock, which prevents fluids from migrating to the surface. Shale and salt domes are common caps

Searching for traps. When petroleum geologists look for oil and gas, they search for geological structures that might serve as traps. In so doing, they rely heavily on reflection seismology. During seismic exploration, explosives, or thumper devices send sound waves through the earth. Reflected sound waves are measured with hydrophones (in water) and geophones (on land). Different layers reflect sound in different ways. With the help of sophisticated software, geophysicists transform seismic data into 3-dimensional maps that show the structure of subsurface rock formations.

For petroleum, there are four major kinds of reservoir traps, three of which are illustrated in Fig. 18.10.

- Anticline traps are, in essence, inverted bowls. They can be symmetrical or asymmetrical. A steep anticline might be called a dome. Anticline traps hold most of the world's conventional crude oil
- Faults are formed at the boundaries of cracks in the earth's crust. The four major kinds of faults are thrust, lateral, normal, and reverse. Thrust and lateral faults are created by horizontal movement. The San Andreas Fault in California is a well-known example of a lateral fault.

To be more specific, the San Andreas is a right-lateral, strike-slip fault. Normal and reverse faults are created by vertical movement and are more likely to create fault traps for petroleum

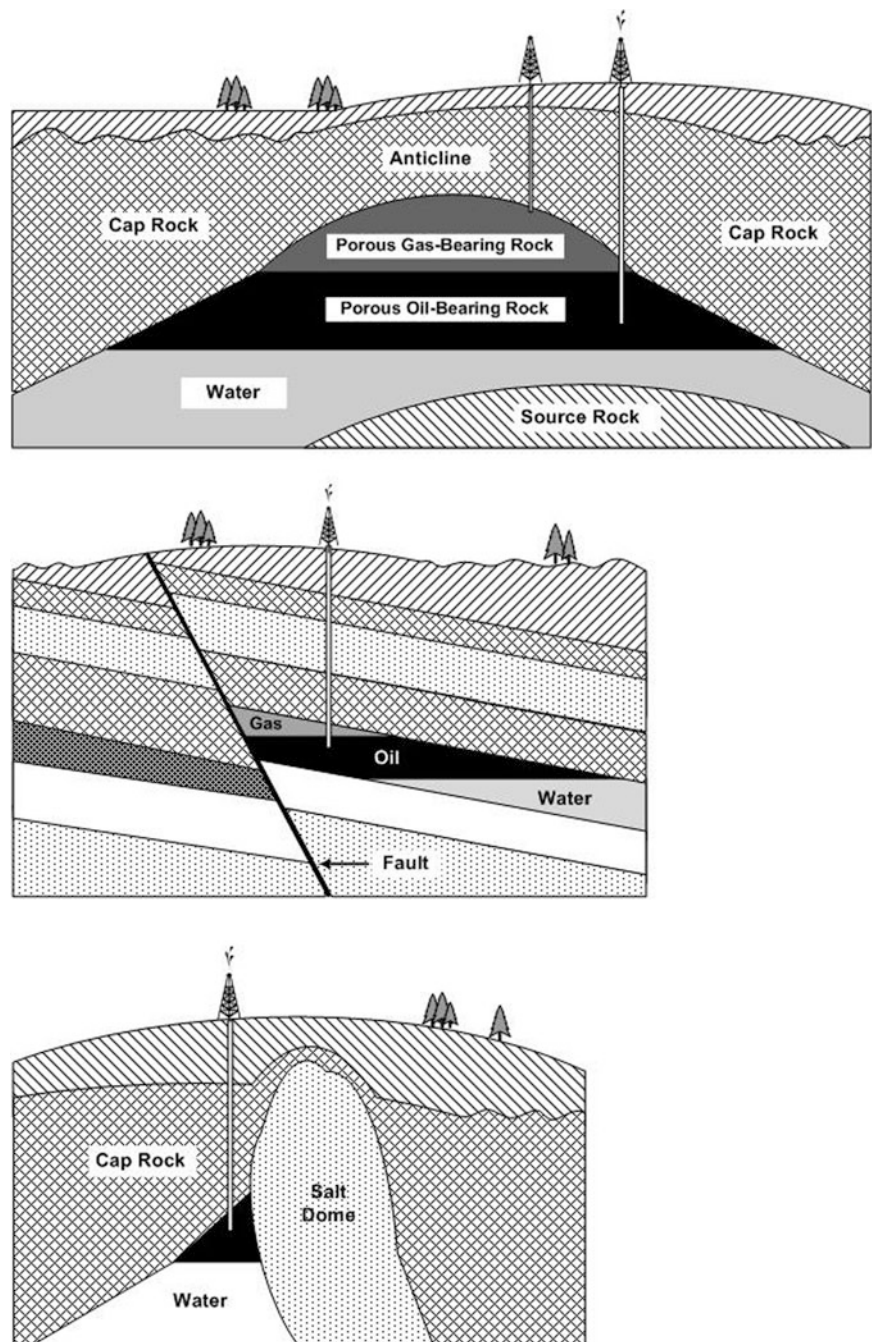
- A salt-dome trap is created when a mass of underground salt is pushed up by underground pressure into a dome. The salt dome breaks through layers of rock and pushes them aside as it rises. The salt is impermeable, and if it abuts porous rock, it can serve as a reservoir cap
- In stratigraphic traps, the reservoir is capped by another reservoir or by layers of rock with lower porosity or permeability

Role of biomarkers in exploration. Biomarkers can indicate the relative amounts of oil and gas in a source rock, the age of a source rock, the environment in which organic matter was deposited, the maturity of a source rock, etc. Often, biomarker data are included in reservoir models of prospective oil fields.

Drilling and Production

Drilling. Key components of a drilling rig are shown in Fig. 18.11. To drill a well, a bit is attached to the end of a drill string, which is comprised of sections of steel pipe that are 30-ft (9 m) long. The drill string is lengthened as the well gets deeper by attaching additional sections of pipe to the top. Drill collars are thick-walled sections of drill pipe at the

Fig. 18.10 Three types of hydrocarbon traps—anticline, fault, and salt dome. As with oil and gas, the water layers are not pools, but water-saturated porous rock



bottom of the drill string; collars apply extra weight to the bit. As the bit cuts through rock, mud is pumped down through the inside of the drill string, out the bit, and up through the space between the drill string and the well bore. Despite its dirty name, drilling mud is a designed blend of fluids, solids, and chemicals. It cools the drill bit and brings rock cuttings back to the surface. The cuttings are removed in shakers, and the fluid goes back to the mud pit, from which it is recycled.

The derrick must be tall enough to accommodate a 90-ft-long “triple” comprised of three sections of pipe. The derrick,

pulleys, and hawser must be robust enough to support the lifting and manipulation of the entire drill string. The kelly is the top joint of a drill string. It has flat sides that fit inside a bushing on the rotary table, which turns the drill string and bit. Note that not all drilling rigs use a kelly system.

A surface blowout is a sudden increase in well pressure resulting in loss of containment and uncontrolled flow of oil and gas into the atmosphere. The blowout preventer (BOP) is a safety valve or other device beneath the floor of the drilling rig. When activated, it stops a blowout by sealing off the top of the well.

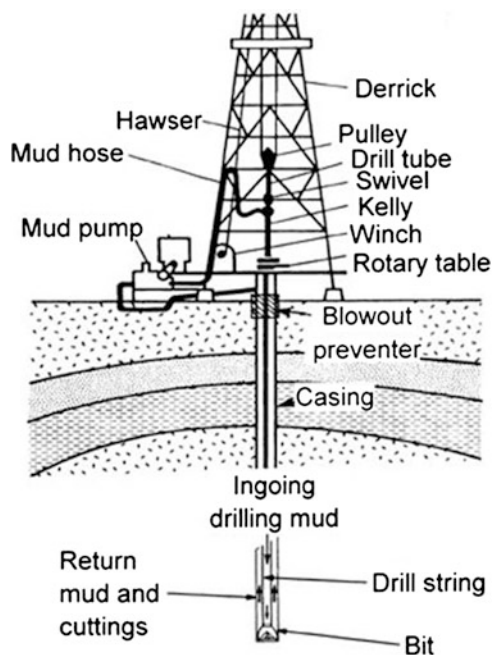


Fig. 18.11 Components of a typical drilling operation [19]

The density of drilling mud is crucial. If the mud density is too low, a well is susceptible to a surface blowout. If the mud density is too high, it can cause an underground blowout—the rupture of the reservoir underground—pushing drilling mud into another formation. Underground blowouts are the most common of all well control problems. Many surface blowouts begin as underground blowouts. Prompt, correct reaction to an underground event can prevent a dangerous and costly surface blowout [20].

Completion. Wells are completed by casing the well bore with steel pipe and cementing the casing into place. Casing prevents the well from collapsing. The outside diameters of casing pipe range from 4.5 to 16 in. (114–406 mm). Cementing is a key step. In a good cement job, the entire space between the casing and the well bore is filled with cement. Centralizers keep the casing from resting against the well bore, which could block the flow of cement, resulting in a poor cement job and increasing the risk of a blowout.

After cementing, perforation guns punch small holes through the casing into the reservoir rock, providing a path for the flow of oil and gas into the well. In open-hole completion, the last section of the well is uncased. Instead, the installation of a gravel pack stabilizes the casing and allows fluids to enter the well at the bottom. After perforation, special acid-containing fluids are pumped into the well to increase porosity and stimulate production. Usually, a smaller diameter tube is inserted into the casing above the production zone and packed into place. This provides an

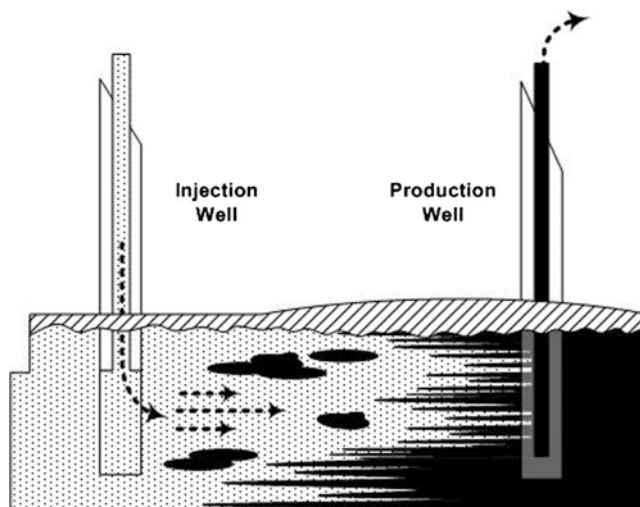


Fig. 18.12 Injection and production wells

additional barrier to hydrocarbon leaks, raises the velocity at which oil flows under a given pressure, and shields the outer casing from corrosive well fluids.

Production. Liquid petroleum may flow on its own due to underground pressure, or it may be forced to the surface by the injection of treated water, natural gas, or CO_2 . Figure 18.12 illustrates using an injection well to stimulate production.

Heavy oil and bitumen are recovered in several ways. They can be dug out with conventional mining techniques, or they can be liquefied by the injection of high-pressure steam. In so-called “huff and puff” operations, production is stopped, either naturally or on purpose. Hot steam is injected into the reservoir and left to soak, usually for a few days. During the soak, heat flows from the steam into the oil and surrounding rock, and the reservoir pressure increases. After the soak, the well is reopened and oil production resumes, at first by natural flow and then by artificial lift. Production decreases over time as the temperature and pressure of the reservoir go down. When the flow of oil drops below a certain limit, the process is repeated.

At surface facilities, notably in Venezuela and Canada, recovered bitumen is diluted with lighter hydrocarbons. The resulting “Dilbit” (diluted bitumen) flows under ambient conditions, so it can be transported conventionally in pipelines and oil tankers.

Kerogen is recovered from oil shale by several methods. From 1985 to 1990, Unocal recovered some 4.6 million barrels of synthetic crude oil from oil shale in a complex mining and upgrading venture at Parachute Creek, Colorado [21]. The plant yielded roughly 40 gal of oil per ton of rock. In the vertical-shaft retort, crushed kerogen-containing shale was pumped up from the bottom of the retort vessel. Hot

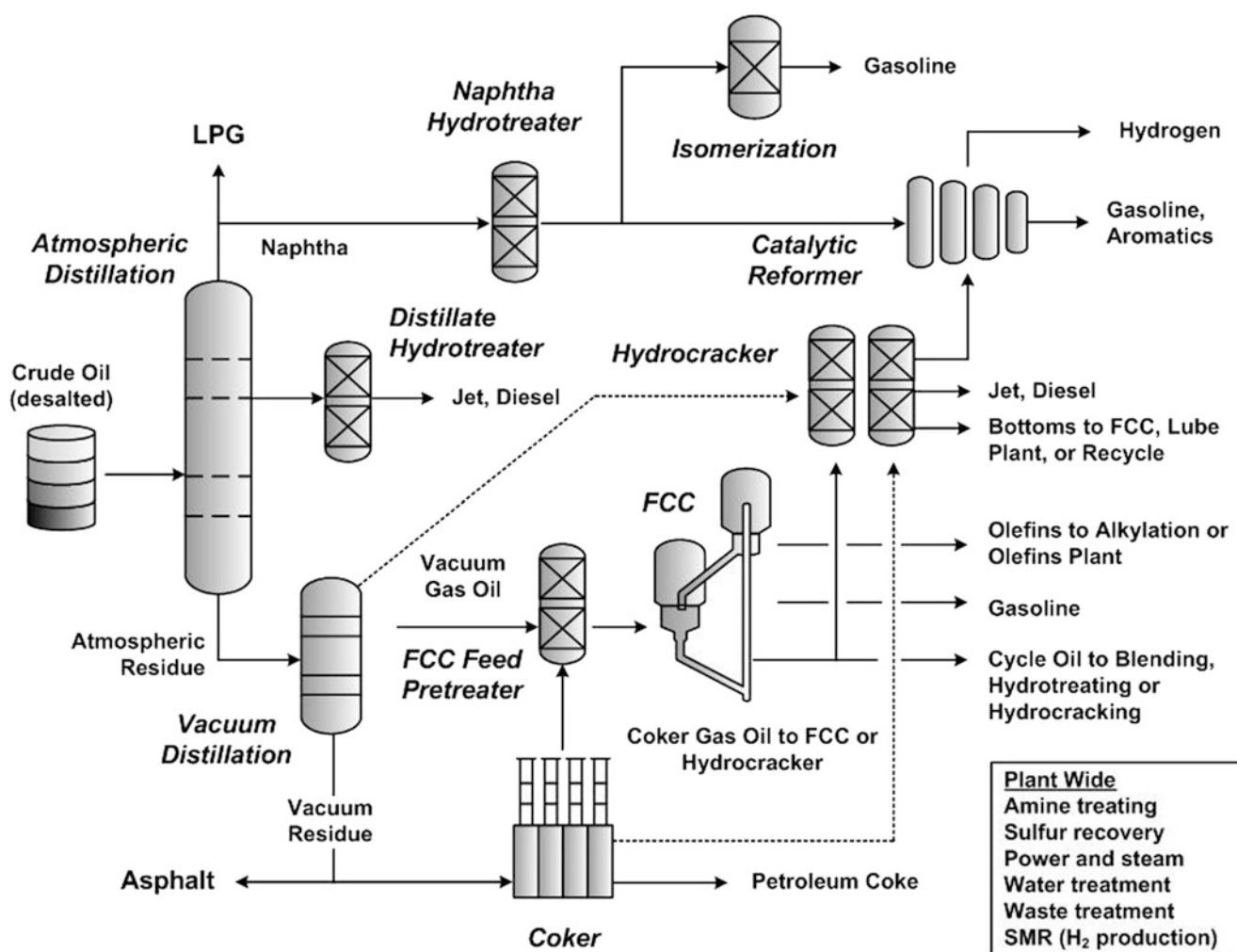


Fig. 18.13 Schematic diagram of a high-conversion petroleum refinery [15, Fig. 10.1]

recycle gas flowed counter-currently downward, decomposing the rock and releasing hydrocarbons. Condensed shale oil was removed from the retort at the bottom. Part of the hot gas was recycled. The rest either was used to produce heat and hydrogen, or recovered as product. The spent shale was removed from the top of the retort, cooled, and stored in pits or returned to the mine. In the reducing environment of the retort, sulfur and nitrogen were converted to H_2S and NH_3 , which were recovered from product gases by conventional means. The plant yielded high-quality synthetic crude oil suitable for further refining in conventional facilities.

Other oil shale processes involve partial combustion, either underground, at the surface, or in shafts drilled horizontally into kerogen-rich formations. From 1972 to 1991, Occidental Petroleum developed an in situ process, in which explosives were used to create underground chambers of fractured oil shale. The oil shale was ignited with external fuel, and air and steam were injected to control combustion. The hot rock fractured and released shale oil, which

was pumped to the surface from a separation sump and collecting well.

Bitumens derived from oil shale and many tar sands contain small-but-significant amounts of arsenic, which are severe poisons for catalysts in refineries.

Refining

Refining petroleum is like cooking crab: you boil it, crack it, and pull out the bits. In a refinery, a given molecule might be boiled and recondensed hundreds of times. Cracking big molecules into small ones is the key to economic success. Pulling out the bits—the removal and disposition of contaminants—improves the cracking processes and protects the environment.

Figure 18.13 shows a simplified schematic diagram for a “typical” North American refinery. The word “typical” is

inside quotation marks, because no two refineries are identical. European and Asian facilities include different process units because they make less gasoline and more middle distillates. They are less likely to employ delayed coking and more likely to use visbreaking for upgrading residue. Plants that produce substantial amounts of lubricants and/or petrochemical monomers include additional sections.

A petroleum refinery transforms the complex tangle of molecules in crude oil into a wide array of products, all of which must meet tight specifications. Listed below are some basic refinery operations.

- Separation
 - Distillation
 - Solvent processes
- Hydrotreating
- Conversion
 - Thermal cracking
 - Thermal hydrocracking
 - Catalytic cracking
 - Catalytic hydrocracking
- Catalytic reforming and isomerization
- Recombination of light intermediates
 - Alkylation
 - Polymerization
- Product treating and blending
- Protecting the environment
 - Gas treating
 - Sulfur recovery
 - SO_x and NO_x abatement
 - Waste treatment
- Related operations
 - Asphalt production
 - Lubricant manufacturing
 - Hydrogen production
 - Hydrogen recovery and purification
 - Production of petrochemical monomers

The Need for Conversion

The demand for petroleum remained relatively flat throughout the last half of the nineteenth Century. In the 1860s the most valuable fraction distilled from crude oil was kerosene. In 1878, thanks to the inventions of Thomas Edison, electric lighting slowly but surely began to displace kerosene as a preferred illuminant. But the advent of the gasoline-powered automobile dramatically increased the demand for petroleum. In addition to increasing overall crude oil demand, the automobile increased demand for naphtha, from which gasoline is derived.

During 1991–2011, the United States consumed, on average, 70 % of its petroleum as gasoline and middle distillates. But as shown in Table 18.7, yields of naphtha plus middle

distillates for four selected (relatively common) crudes range from 33.8 to 61.8 %. This leaves sizeable supply/demand gaps, which create a sizeable light-product/heavy-product price differential. A common measure of this differential is the “heating oil crack spread.” Since 2010, crack spreads ranged between \$6 and \$25 per barrel. In January 2011, they exceeded \$24 per barrel [22]. At that differential, for a refinery that processes 200,000 barrels of oil per day, 30 % conversion is worth about \$1.4 million per day—about \$500 million per year.

In response to such huge incentives, refiners, and licensors have developed an array of processes for converting heavy products into light ones. Many of these are described below. But before discussing the hardware, let’s look at the chemistry around which the hardware is built.

Petroleum Refining Chemistry

“Cracking” and “pulling out the bits” involve the chemical reactions listed below.

- Hydrotreating and saturation
 - Saturation of aromatics (ASAT) and olefins (OSAT)
 - Hydrodesulfurization (HDS)
 - Hydrodenitrogenation (HDN)
 - Hydrodeoxygenation (HDO)
 - Hydrometalation (HDM)
- Cracking (making little ones out of big ones)
 - Thermal cracking
 - Catalytic cracking
 - Hydrocracking (catalytic and thermal)
- Dehydrogenation, isomerization (no change in carbon number)
- Alkylation, polymerization (making big ones out of little ones)
- Acid/base processes: amine treating, caustic scrubbing
- Mercaptan oxidation (Merox)

Hydrotreating reactions: saturation of olefins. On a macro scale, the saturation of olefins is rapid and essentially irreversible. It releases considerable heat.

Hydrotreating reactions: saturation and condensation of aromatics and polyaromatics. Figure 18.14 provides examples of the reversible saturation of aromatics and polyaromatics. Figure 18.15 [8] summarizes thermodynamic calculations for the competition between the saturation of naphthalene and the condensation of naphthalene with *o*-xylene to form chrysene. At high pressures and low temperatures, equilibrium favors saturation. At low pressures and high temperatures, equilibrium favors dehydrogenation. At high-enough temperatures, equilibrium favors condensation (Fig. 18.16).

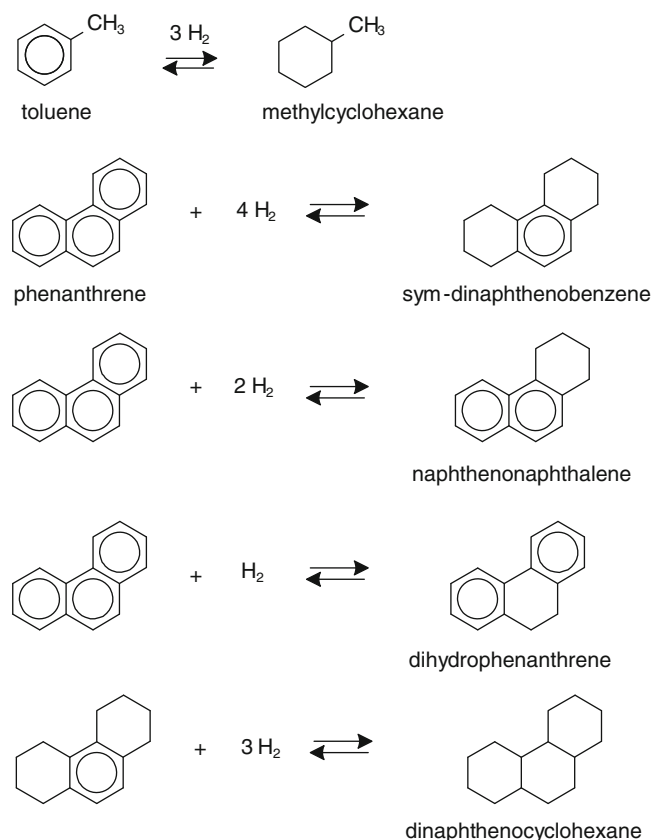


Fig. 18.14 Saturation of aromatics and polyaromatics

Figure 18.6 shows the so-called zig-zag mechanism for the production of large polyaromatics by adding 2-carbon and 4-carbon species to smaller polyaromatics. The condensation of large polyaromatics via the Scholl reaction can lead eventually to coke formation [25].

Figure 18.17 shows a mechanism for the one-at-a-time build up of rings on a nucleus of coke. The mechanism includes the following steps, all of which are to some extent reversible:

- Hydrogen abstraction by gas-phase radicals
- Addition of radicals to the coke surface
- Reaction of a gas-phase olefin with a radical on the surface
- Reaction of a gas-phase radical with an olefin group on the surface
- Cyclization
- Dehydrogenation

Hydrotreating and hydrocracking units operate in the crossover region between 315 and 425 °C (600 and 800 °F). Per Fig. 18.15, at temperatures below the crossover region, saturation is favored. Temperatures above crossover favor aromatics.

Hydrotreating reactions: HDS. Figure 18.18 shows representative hydrodesulfurization (HDS) reactions. Note that

for sulfur removal from the first three reactants, the mechanism is direct. That is, the sulfur-containing molecule interacts with an active site on the catalyst, which removes the sulfur atom and replaces it with two hydrogen atoms. Additional hydrogen converts the sulfur atom into H_2S , which desorbs from the catalyst, leaving behind a regenerated active site.

For the fourth reactant—4,6-dimethyldibenzothiophene (4,6-DMDBT)—the reaction proceeds via both a direct and an indirect route. The 4,6-DMDBT molecule is planar, and the two methyl groups are adjacent to the sulfur atom. This protects the sulfur atom from active sites on the catalyst, thereby inhibiting direct HDS. In the indirect route, saturating one of the aromatic rings that flank the sulfur atom converts the planar structure into a puckered arrangement with tetrahedral C–C bonds. This puckering rotates one of the inhibiting methyl groups away from the sulfur atom, giving it better access to the catalyst.

Making ultra-low-sulfur diesel (ULSD), in which the sulfur content is less than 10–15 wppm, requires severe hydrotreating, after which the only remaining sulfur compounds are the above-mentioned 4,6-DMDBT and other di- and trimethyl dibenzothiophenes. Because the removal of sulfur from these compounds is more facile after prior saturation, the crossover phenomenon affects the production of ULSD significantly, so much so that it governs the design of commercial units.

Hydrotreating reactions: HDN. Figures 18.19 and 18.20 show representative HDN reactions. Figure 18.19 illustrates the mechanism for the HDN of quinoline. As with sulphur removal from hindered DMDBTs, the crossover phenomenon is important for deep HDN, because nitrogen removal requires prior saturation of an aromatic ring adjacent to the nitrogen atom.

Hydrotreating reactions: HDO. In feeds to industrial hydroprocessing units, oxygen is contained in organic acids, ethers, peroxides, and other compounds. Some form by reacting with air during transportation and storage of crude oil, distillates, and cracked stocks generated by delayed coking and Fluid catalytic cracking (FCC) units (see below). Hydrodeoxygenation (HDO) proceeds rapidly, so rapidly that it can cause problems with excessive heat release. Also, oxygen compounds can form gums and polymers, which inhibit flow and increase pressure drop.

Hydrotreating reactions: HDM. Metals such as nickel and vanadium are present in high-boiling fractions, mostly in asphaltenes. Asphaltenes are mixtures of waxy solids with porphyrins (Fig. 18.9). Corrosion generates soluble iron, and entrained salt brings in alkali and alkaline earth metals,

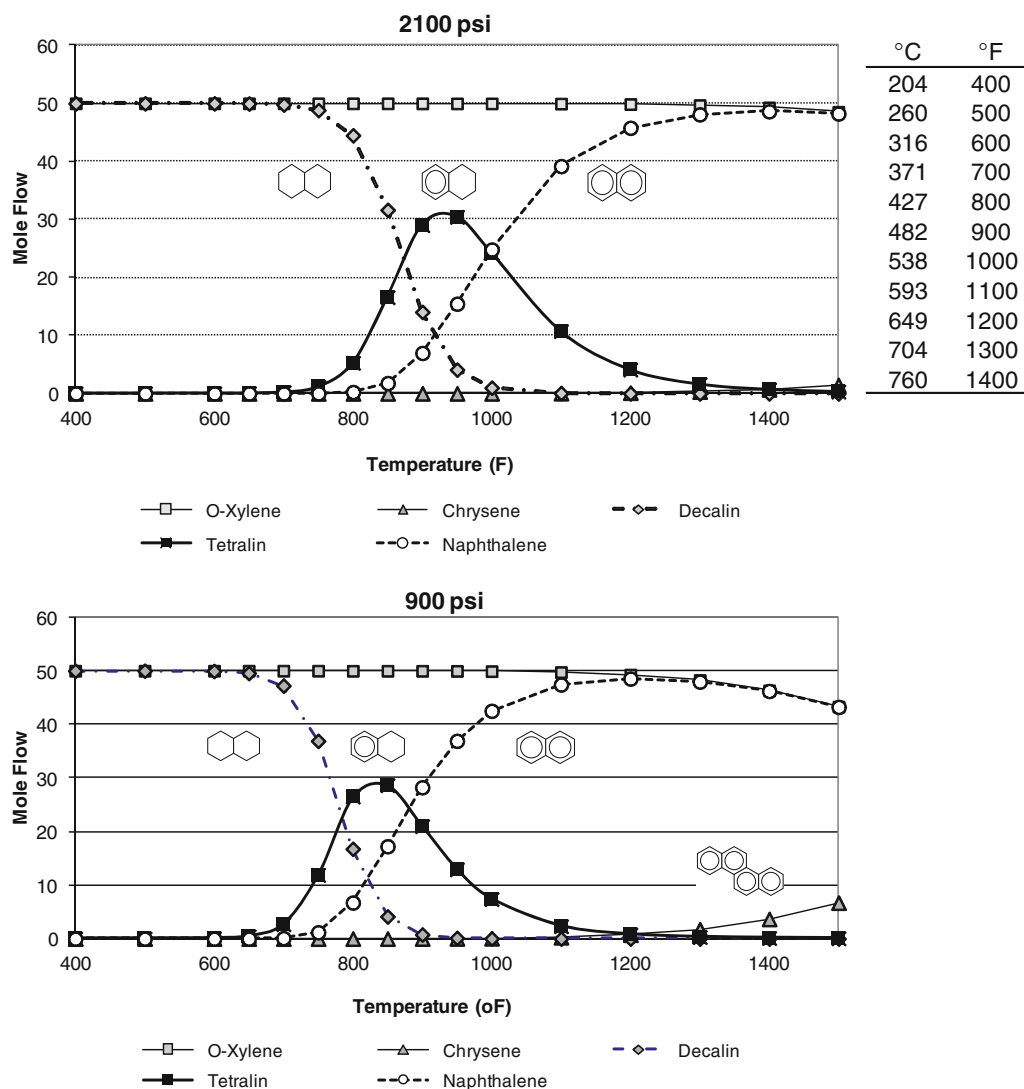


Fig. 18.15 Thermodynamic calculations illustrating the competition between the saturation and the condensation of polyaromatics [23]. Data for the graphs were generated by Aspen Plus for a six component

system comprising naphthalene ($C_{10}H_8$), tetralin ($C_{10}H_{12}$), decalin ($C_{10}H_{18}$), *o*-xylene (C_8H_{10}), chrysene ($C_{18}H_{12}$), and hydrogen (not shown)

primarily sodium and calcium. Synthetic crudes from oil sands and oil shale tend to contain small-but-significant amounts of arsenic. Silicones are added to crude oil to facilitate flow through pipelines. Silicones are also used to control foaming in delayed coking units.

All of these metals poison refinery catalysts. Refiners remove them by hydrotreating over special wide-pore guard catalysts. Guard materials remove some contaminants by chemisorption. Other contaminants, such as Ni, V, and soluble Fe, are removed by HDM reactions. HDM converts the metals into sulfides, which adhere to the guard material.

Conversion. Table 18.10 illustrates a fundamental aspect of conversion. For a given class of hydrocarbons, “lighter” means a lower molecular weight, lower boiling point, lower density, and a higher hydrogen-to-carbon ratio (H/C).

Methane, the lightest hydrocarbon, has an H/C ratio of 4.0. Benzopyrene has an H/C ratio of 0.6. The H/C ratio of common crude oils ranges from 1.5 to 2.0, while the H/C ratio for asphaltenes is about 1.15.

Some conversion processes—FCC, thermal cracking, and deasphalting—increase the H/C ratio by rejecting carbon. Hydrotreating and hydrocracking increase the H/C ratio by adding hydrogen. In this context, “rejecting carbon” does not mean that a few carbon atoms are removed from every large molecule. Rather, it means that heavy molecules are split (“cracked”) into lighter molecules with higher H/C ratios and heavier molecules with lower H/C ratios.

Conversion: definition. Refiners define conversion as a change in boiling point. The goal of a conversion process is to crack material that boils above a particular cutpoint into

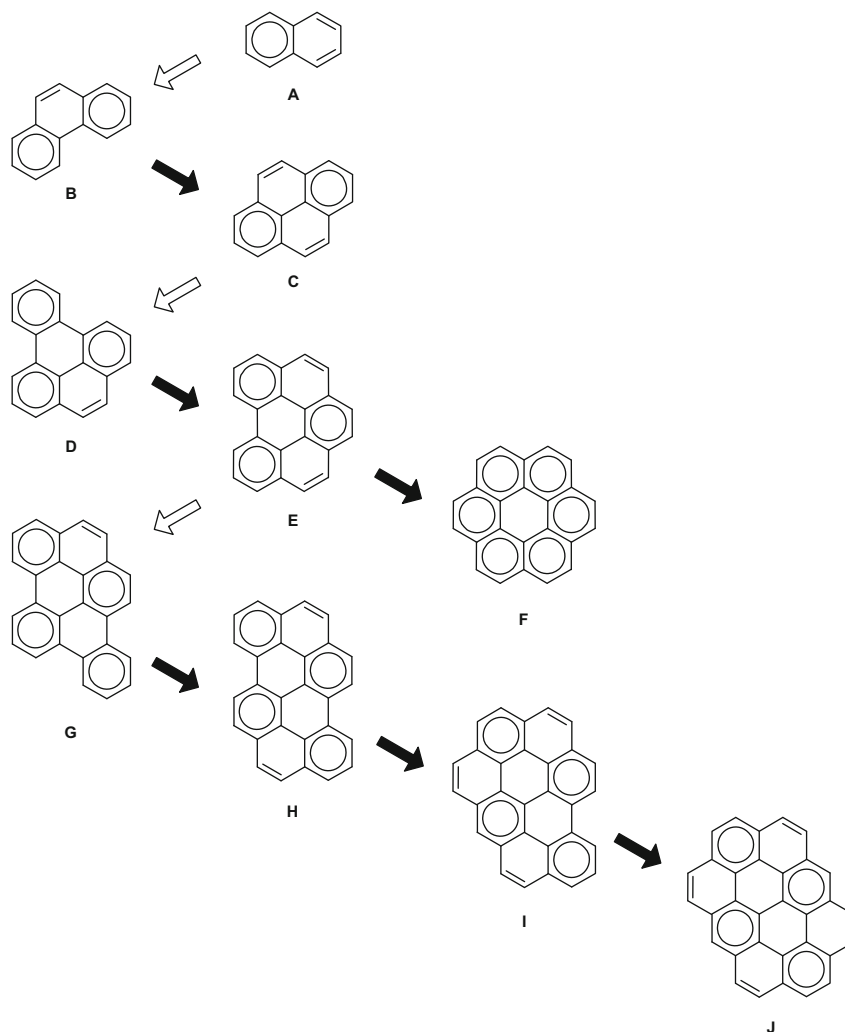


Fig. 18.16 Zig-zag mechanism for the condensation of polyaromatics by sequential addition of 2-carbon and 4-carbon units [24]. The isomers shown are (a) naphthalene, $C_{10}H_8$; (b) phenanthrene, $C_{14}H_{10}$; (c) pyrene, $C_{16}H_{10}$; (d) benzo[e]pyrene, $C_{20}H_{12}$; (e) benzo[ghi]perylene, $C_{22}H_{12}$; (f) coronene, $C_{24}H_{12}$; (g) dibenzo[b,pqr]perylene,

$C_{26}H_{14}$; (h) benzo(pqr)naphtho(8,1,2-bcd)perylene, $C_{28}H_{14}$; (i) naphtho[2',8',2,4]coronene, $C_{30}H_{14}$; and (j) ovalene, $C_{32}H_{14}$. Note how the H/C ratio goes down as condensation increases, from 0.8 for naphthalene to 0.4375 for ovalene

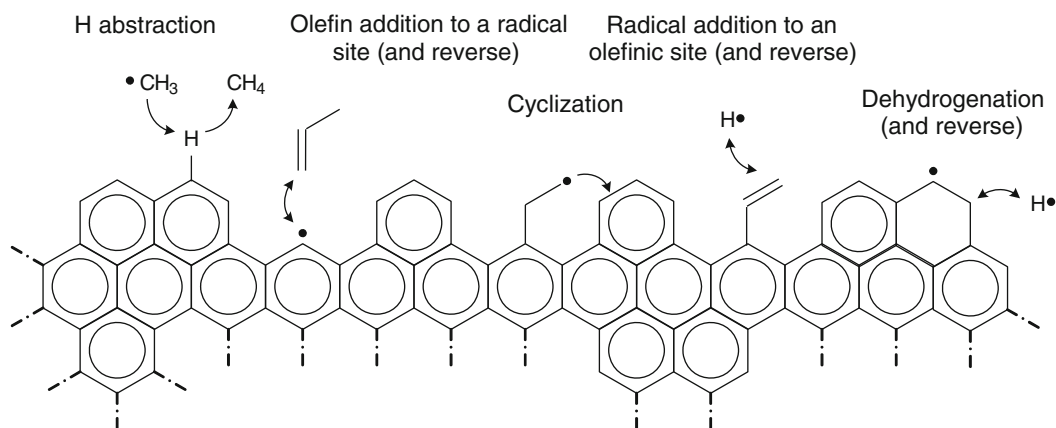
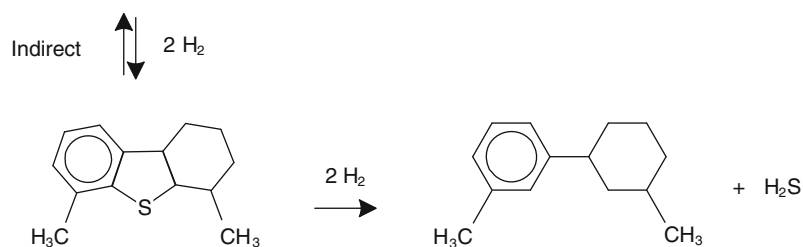
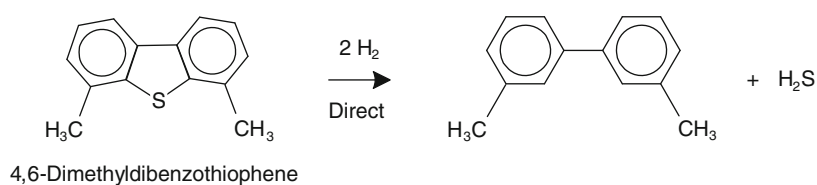
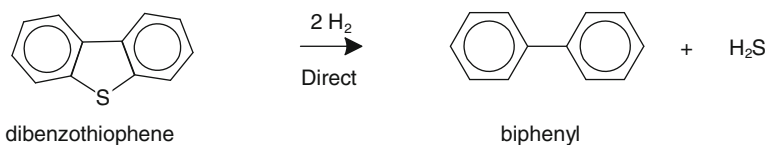
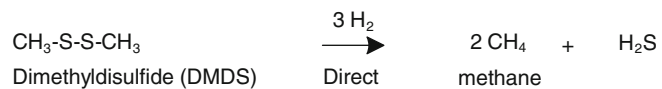
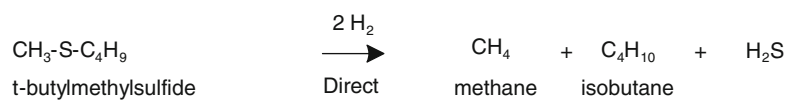
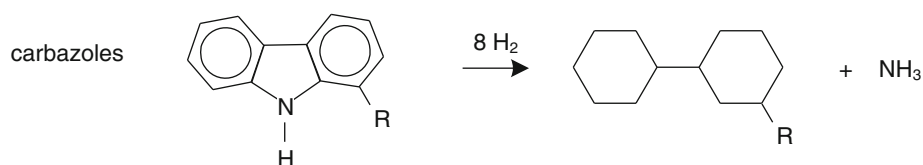
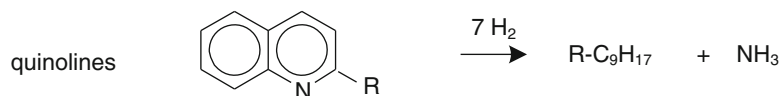


Fig. 18.17 Mechanism for the addition of rings to a nucleus of coke [26]

Fig. 18.18 Representative hydrodesulfurization (HDS) reactions**Fig. 18.19** Representative hydrodenitrogenation (HDN) reactions

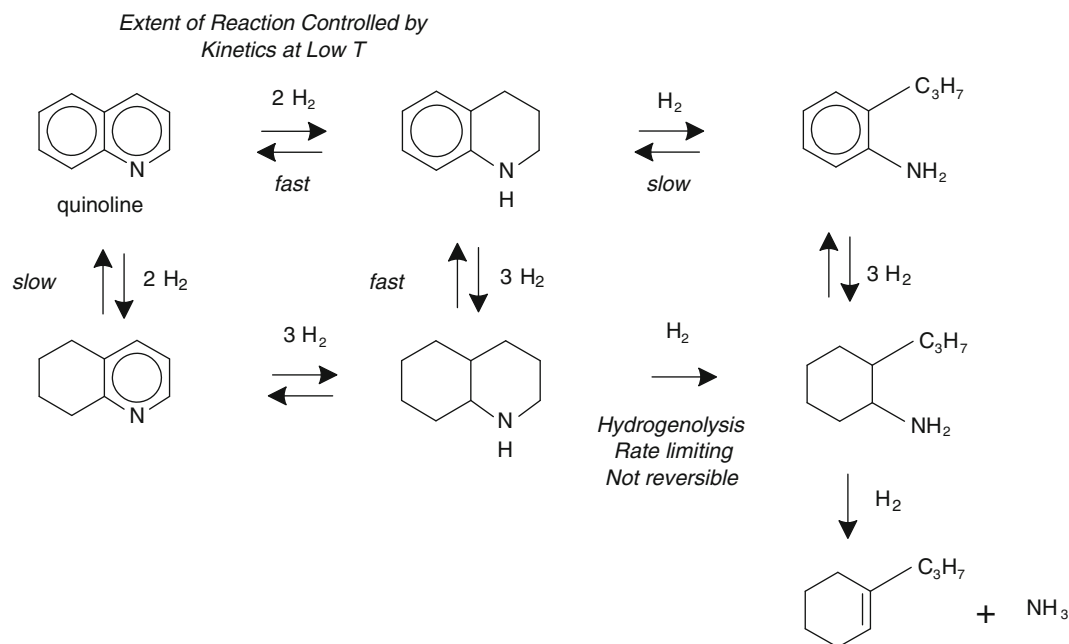


Fig. 18.20 Mechanism for the HDN of quinoline [27]

Table 18.10 Molecular weight, H/C, and boiling points for selected hydrocarbons

Compound	Molecular weight	Formula	H/C	Boiling point	
				°C	°F
Paraffins					
Methane	16.04	CH ₄	4.0	−164	−263.2
Ethane	30.07	C ₂ H ₆	3.0	−88.6	−127.5
Propane	44.10	C ₃ H ₈	2.67	−42.1	−43.7
Butane (iso)	58.12	C ₄ H ₁₀	2.50	−6.9	19.6
Octane (iso)	114.23	C ₈ H ₁₈	2.25	99.2	210.6
Cetane (n)	226.44	C ₁₆ H ₃₄	2.13	287	548.6
Aromatics					
Benzene	78.11	C ₆ H ₆	1.0	80.1	176.2
Naphthalene	128.17	C ₁₀ H ₈	0.8	218	424.4
Benzopyrene	252.32	C ₂₀ H ₁₂	0.6	—	—

material that boils below that particular cutpoint. A typical cutpoint for naphtha-oriented conversion is 400 °F (204 °C), while a typical cutpoint for diesel-oriented conversion is 650 °F (343 °C). The equation for conversion is simple:

$$\text{Conversion} = P/\text{FF} * 100\%$$

where P = the amount of material in the product that boils below the chosen cutpoint and FF = the total amount of fresh feed. In “true conversion” calculations, the amount of P in the FF prior to conversion is subtracted from the numerator.

Conversion Chemistry

Thermal cracking. Figure 18.21 outlines the mechanism for the thermal cracking of hydrocarbons. This chain-reaction mechanism includes the following steps:

1. Chain reaction initiation: Free radicals form due to the direct thermal rupture of a carbon–carbon bond
2. Chain reaction propagation: A small radical reacts with a large hydrocarbon to give a small alkane and a large primary radical
3. Cracking: The large primary radical decomposes into ethylene and a primary radical with two fewer carbon atoms
4. Isomerization: A primary radical isomerizes into a secondary radical
5. Cracking: A secondary radical decomposes into propylene and a primary radical with three fewer carbon atoms
6. Radical addition: A radical reacts with an olefin to produce a larger radical. Addition reactions such as this eventually generate coke
7. Chain reaction termination: Two radicals react to produce an olefin and hydrogen. The olefin can undergo further reactions per Step 6
8. Chain reaction termination: Two radicals react to produce a large alkane
9. Chain reaction initiation: In this case, the initiator is external, e.g., an organic peroxide

The free-radical mechanism is consistent with the fact that thermal cracking produces significant amounts of hydrogen, methane, ethane, ethylene, and higher olefins.

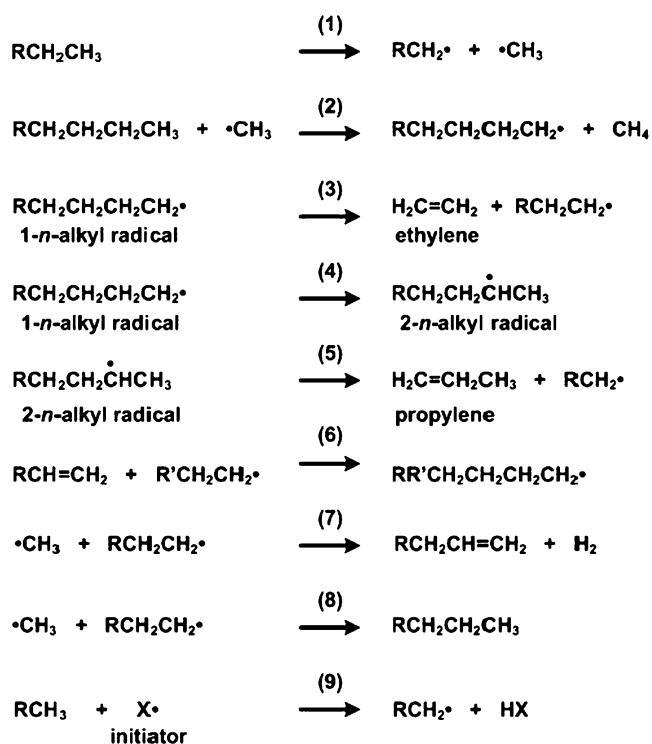
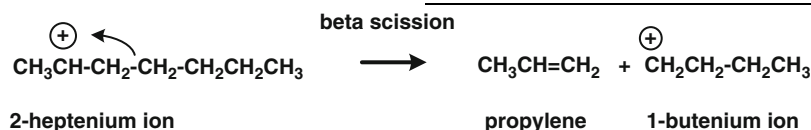


Fig. 18.21 Thermal cracking mechanism [28]

Real-world feeds contain sulfur, nitrogen, oxygen, and other hetero atoms. These form H_2S , ammonia, and water, along with a wide range of hetero-atom organic compounds. Consequently, products (including the water) from delayed coking units contain sulfur and nitrogen compounds.

Catalytic cracking. Figure 18.22 illustrates the mechanism for the catalytic cracking of paraffins. The catalysts contain strong acid sites, and the reactions involve carbocations (also known as carbenium ions or carbenium ions.)

Beta scission is illustrated below. The C–C bond that breaks during acid-catalyzed cracking is two carbons away from the positively charged carbon atom. Also, terminal (1°) carbocations ions are very reactive and quickly rearrange into 2° or 3° carbonations. Therefore, the smallest stable cracked fragment is a C_3 moiety.



- Abstraction of a hydride ion from *n*-heptane by a Lewis acid site to make a carbocation
- Addition of a proton to a heptene molecule to make a carbocation, which may or may not be the same as the one produced by Step 2. This reaction is reversible. At any point in the mechanism, a C_3 or higher carbocation can undergo proton elimination to form an olefin
- Cracking via β scission. This means that cracking occurs two carbon atoms away from the carbon atom holding the positive charge
- Rearrangement (alkyl shift). As an alternative to Step 4, carbocations can rearrange to form more-stable branched intermediates, which lead to branched products. This explains why the products of catalytic cracking are rich in branched isomers. (In a 3° carbocation, the carbon with the positive charge is attached to three other carbon atoms. In a 2° carbocation, the positive carbon is attached to two other carbons. In a 1° “terminal” carbocation, the positive carbon is attached to only one other carbon. The order of stability is: $3^\circ > 2^\circ > 1^\circ$.)
- Double-bond shift. After an olefin undergoes double-bond shift, the new olefin can react as before with an acid site per Step 3. It can also undergo alkylation by reacting with a carbocation (Fig. 18.21)

Isomerized carbocations can undergo β scission per Step 4. Catalytic cracking units also make aromatics and other heavy products via cyclization, alkylation, and polymerization of intermediate olefins. Figure 18.23 shows the kinds of ring-formation reactions that lead to the generation aromatics and polyaromatics during catalytic cracking. As shown in Fig. 18.16, polyaromatics can grow into larger polyaromatics, which eventually can form coke.

Catalytic hydrocracking. In many respects, the mechanism for catalytic hydrocracking is the same as for catalytic cracking. The main differences are:

- During hydrocracking, aromatic rings are saturated into naphthenic rings, which can then be cracked per the reactions in Fig. 18.24
- The presence of high-pressure hydrogen and metal sites favor the saturation of olefin intermediates. This inhibits

The main steps in catalytic cracking are:

- Dehydrogenation to form a heptene molecule. The reaction is catalyzed by metal sites on the catalyst. It is also reversible. At any point, an olefin can undergo hydrogenation to form a paraffin

ring-formation and ring-growth reactions

For the hydrocracking of fluorene (C_{13}H_9), Lapinas et al. [30] propose a mechanism that might apply generally to the hydrocracking of polyaromatics. In simplified form, Fig. 18.24 shows the sequence of reactions by which

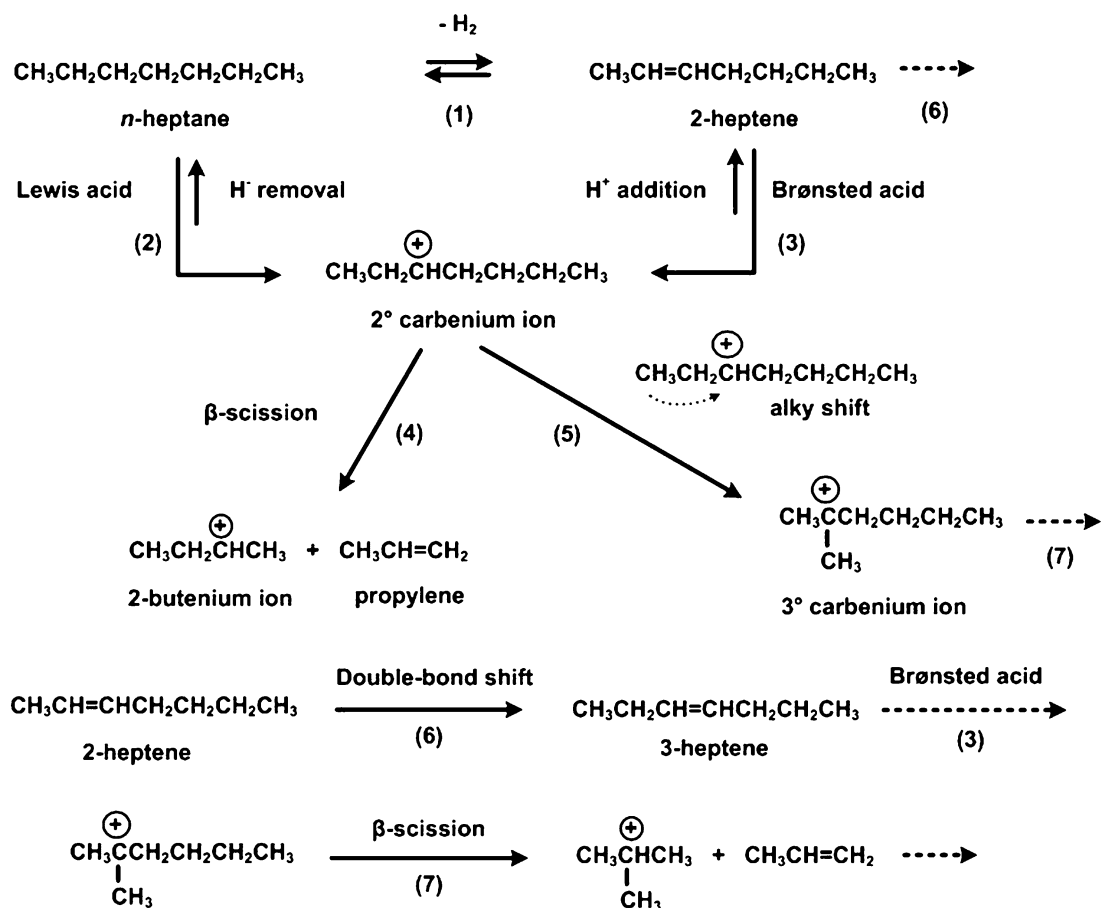
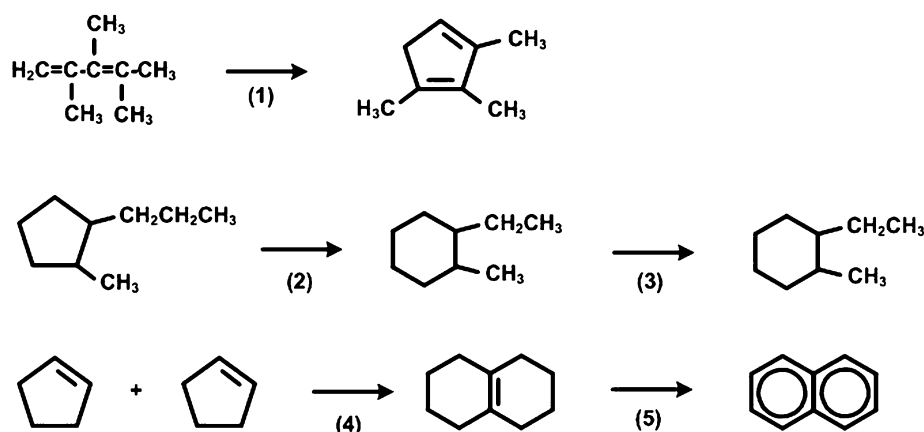
Fig. 18.22 Catalytic cracking of *n*-heptane [28]

Fig. 18.23 Ring-formation reactions during catalytic cracking [29]

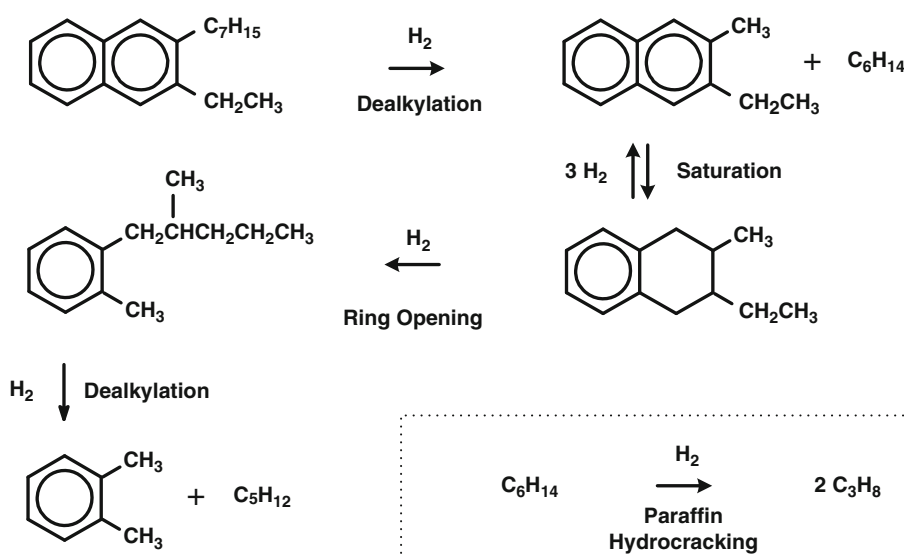
hydrocracking converts a heptyl ethyl naphthalene isomer into lighter compounds. The reactions include:

- Removal of part of a side chain by dealkylation
- Saturation of an aromatic ring
- Isomerization of the saturated ring

- Opening the saturated ring
- Paraffin hydrocracking

The first dealkylation reaction removes hexanes, not heptanes. The ethyl group is not removed, because (a) the production of methane by the β -scission of a two-carbon

Fig. 18.24 Simplified reaction sequence for the hydrocracking of polyaromatics



C–C bond isn't possible, and (b) it is difficult to form the required intermediate from an aromatic ring stabilized by resonance energy.

Comparison of catalytic and thermal cracking. Based on [28], Table 18.11 provides a comparison between the catalytic and thermal cracking processes:

Alkylation chemistry. Figure 18.25 shows the mechanism for the alkylation reaction of 2-butene with isobutane. During the process, 2-butene can isomerize. Reactions 2a and 2c show how different isomers lead to different products. Reaction 4 illustrates how additional alkylation reactions could eventually produce sludge, coke, and other heavy products.

Catalytic reforming chemistry. Figure 18.26 shows the reactions involved in catalytic reforming, the purpose of which is to transform naphthenes and C_6 to C_{11} paraffins into aromatic compounds. The process yields considerable amounts of hydrogen, which is used in hydrotreaters, hydrocrackers, and other units requiring hydrogen. In contrast to hydrocracking, catalytic reforming operates at low pressure and high temperature, which favors production of aromatics. The conversion of cyclopentanes into cyclohexanes (Reaction 3) is a key step in the production of benzene and alkylbenzenes.

Isomerization chemistry. In refineries, isomerization units convert n -paraffins into isoparaffins. In C_4 isomerization, n -butane is converted to isobutane in a two-stage process, which employs HCl-promoted $AlCl_3$ for the first stage and a supported noble metal catalyst in the second stage. C_5/C_6 isomerization converts normal pentanes and hexanes and 1° hexanes into highly branched isomers.

Table 18.11 Comparison of product yields for catalytic and thermal cracking processes

Process	Type	Product characteristics
FCC	Catalytic cracking	C_1 and C_2 : low Branched/normal paraffin ratio: high Light olefin yields: significant Heavy olefin yields: low Aromatics: higher than feed Coke formation: high Olefin reactivity: higher than paraffins Alkyl aromatics: scission next to the ring
Hydrocracking	Catalytic cracking in the presence of hydrogen	C_1 and C_2 : low Branched/normal paraffin ratio: high Olefins: removed by pretreating Aromatics: lower than feed Coke formation: minimal Alkyl aromatics: scission next to the ring
Coking visbreaking	Thermal cracking	C_1 and C_2 : high Branched/normal paraffin ratio: similar to feed Olefin production: high Aromatics: low Coke formation: high Olefin reactivity: similar to paraffins Alkyl aromatics: scission within the side chain

Based in part on Table A in [28]

During lube stock production, heavy n -paraffins are converted into isoparaffins with minimal cracking over silica-alumina phosphate (SAPO)-based catalysts or similar materials.

Fig. 18.25 Alkylation of 2-butene by isobutane [31]

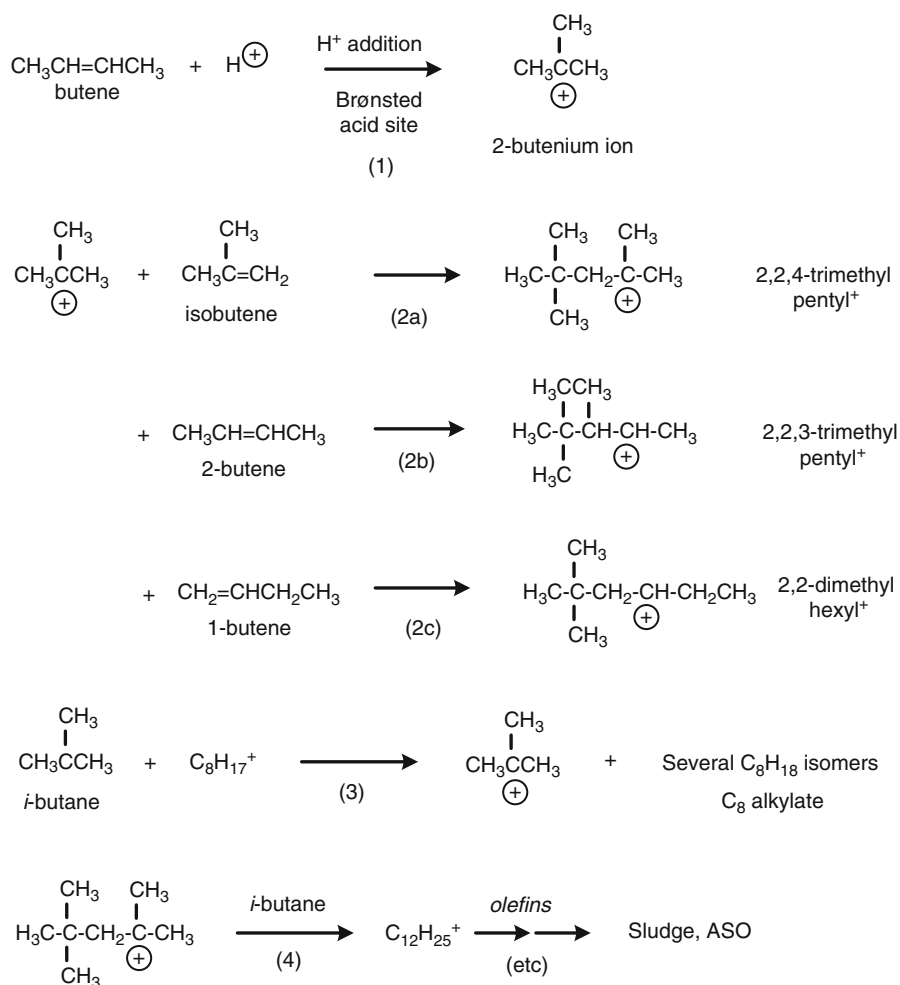
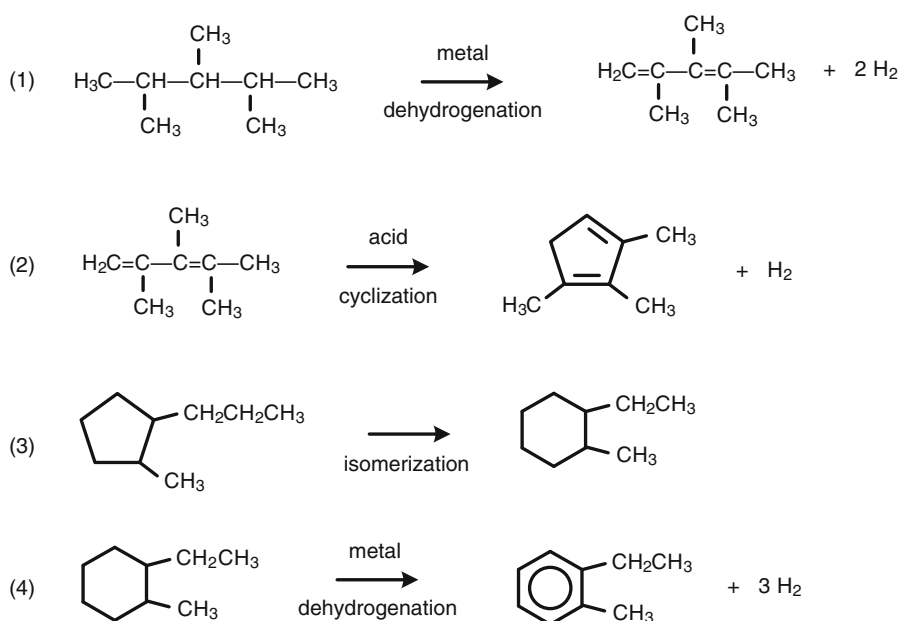
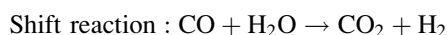


Fig. 18.26 Catalytic reforming reactions



Olefin isomerization converts straight-chain C_4 – C_6 olefins into corresponding iso-olefins.

Steam-hydrocarbon reforming (SMR) chemistry. Steam-hydrocarbon reforming produces hydrogen through the reaction of steam with light hydrocarbons at very high temperatures—around 1,500 °F (816 °C). The hydrocarbon feed usually is methane, so even though other hydrocarbons are used, a generic term for the process is steam-methane reforming (SMR). The product of the initial reaction is a mixture of H_2 , CO, CO_2 , residual methane, and in some cases traces of other hydrocarbons. The initial product goes to one or more shift reactors, where the shift reaction between H_2O and CO yields CO_2 and additional hydrogen.

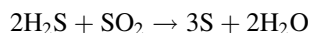
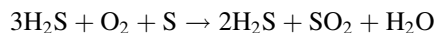


In older units, residual CO was removed by methanation over a nickel-based catalyst, and residual CO_2 was removed by adsorption with activated molten potassium carbonate (Benfield process). The product hydrogen contained up to 5 % methane.



In newer units, pressure-swing adsorption (PSA) removes nearly all contaminants, yielding a product containing 99.99 % hydrogen.

Sulfur recovery (Claus process) chemistry. Claus-process sulfur recovery units burn hydrogen sulfide in just enough air to form a mixture of H_2S and SO_2 in a 2:1 molar ratio. In downstream beds of alumina catalyst, the H_2S reacts with the SO_2 to form elemental sulfur and water.

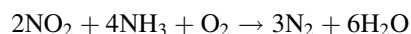
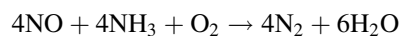


The product sulfur can include many different isomers of S_x .

Acid/base treating reactions. Several processes entail seemingly simple acid–base reactions. Amine treating removes acid gases— H_2S and CO_2 —from fuel gas and off-gas streams. In some hydrotreaters and hydrocrackers, high-pressure amine units remove H_2S from the recycle gas. Caustic scrubbers are used in several ways, including

removing the last traces of H_2S from the hydrogen used for processes that are highly sulfur sensitive.

Catalytic NO_x removal chemistry. Selective catalytic reduction (SCR) removes nitrogen oxides (NO_x) by reaction with ammonia to produce nitrogen via the following main reactions. Secondary reactions involve sulfur oxides and ammonium sulfates.



Petroleum Refining Processes

Some passages in this section are abstracted from [8] and are used with kind permission from the publisher: Springer Science+Business Media, Inc. The *2011 Refining Process Handbook* published by *Hydrocarbon Processing* is an excellent source of additional information on individual processes.

Crude oil pretreatment. Crude oil comes from the ground mixed with a variety of substances: gases, water, salt, and dirt. These must be removed before the crude can be transported effectively and refined without undue fouling and corrosion. Some cleanup occurs in oil fields. In refineries, crude desalting units provide subsequent cleanup.

A field separator is often no more than a large covered vessel that provides enough residence time for gravity separation into four phases: gases, crude oil, water, and solids. Generally, the crude oil floats on the water. The water is withdrawn from the bottom and is disposed of at the well site. Gases are withdrawn from the top and piped to a natural gas processing plant or reinjected into the reservoir to maintain well pressure. Crude oil is pumped either to a refinery through a pipeline or to storage to await transportation by other methods.

At the refinery, the crude is treated with hot water in one or more desalters. Desalters employ either chemical or electrostatic precipitators to remove dissolved salts and collect remaining solids. In chemical desalting, water and surfactants are added to the crude, heated to dissolve salts and other impurities, then sent to a settling tank, where the water and oil separate. In electrostatic desalting, chemicals are replaced with a strong electrostatic charge, which drives the separation of water from oil.

If the crude isn't desalted, residual solids can clog downstream equipment and deposit on heat-transfer surfaces, thereby reducing heat-transfer efficiency. Salts can induce corrosion in major equipment and deactivate catalysts.

Fig. 18.27 Two-stage crude oil distillation unit [8], Fig. 9, with kind permission from Springer Science+Business Media, Inc

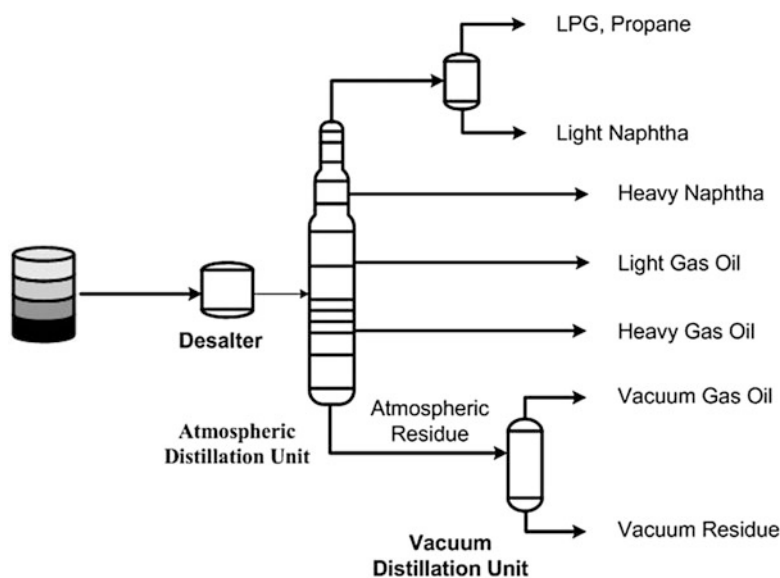


Figure 18.27 presents an overview of a typical two-stage crude oil distillation unit (CDU), and Fig. 18.28 shows an atmospheric distillation tower with bubble-cap internals.

Before reaching the atmospheric tower, desalted oil goes through a network of preheat exchangers to a fired heater, which brings the temperature up to 657–725 °F (347–385 °C). If the oil gets much hotter than this, it starts to crack, generating carbon. The carbon would deposit inside the pipes and equipment through which the oil flows.

The hot crude enters the tower just above the bottom. Steam is added to enhance separation; it does so largely by decreasing the vapor pressure of hydrocarbons in the column. When it enters the tower, most of the oil vaporizes. Unvaporized oil drops to the bottom of the tower, where it is drawn off. The vapors rise through the distillation trays, which contain perforations, bubble caps, downcomers, and/or modifications thereof. Each tray permits vapors from below to bubble up through the relatively cool condensed liquid on top of the tray. This vapor/liquid contacting knocks heavy material out of the vapor. Condensed liquid flows down through a pipe (downcomer) to the hotter tray below, where the higher temperature causes re-evaporation. A given molecule evaporates and condenses many times before finally leaving the tower.

Products are collected from the top, bottom, and side of the column. Side-draw products are taken from trays where the temperature corresponds to the cutpoint for a desired product. Some of the side-draws can be returned to the tower as a pump-around or pump-back stream to control tower temperatures, improve efficiency, and further enhance separation. Reflux plays a major role in controlling temperature at the top of the tower, where gases and light naphtha are drawn off overhead.

The bottom stream from the main fractionator is called atmospheric bottoms, atmospheric residue, or long resid. It goes to a second fired heater, where the typical outlet temperature is about 750–775 °F (400–413 °C). From the second heater, the atmospheric residue goes to a vacuum tower. Steam ejectors reduce the absolute pressure to about 7.0 psia (0.5 bara). Under vacuum, hydrocarbons vaporize at lower temperatures. Thus, molecules with normal boiling points above 650 °F (343 °C) can be vaporized at lower temperatures, where they are less likely to undergo thermal cracking.

Products from the crude distillation unit go to other process units, as shown in Table 18.12.

Solvent refining. Solvent refining processes include solvent deasphalting, solvent extraction, and deoiling/dewaxing processes.

Solvent deasphalting takes advantage of the fact that aromatic compounds are insoluble in paraffins. Propane and *n*-pentane are used to precipitate asphaltenes from residual oils. The deasphalted oil (DAO) is sent to hydrotreaters, FCC units, hydrocrackers, or fuel-oil blending. In FCC units, DAO is easier to process than the corresponding straight-run residue. This is because the asphaltenes in straight-run residue easily form coke and often contain catalyst poisons such as nickel and vanadium; the asphaltene content of DAO is (by definition) almost zero. In hydrocrackers, DAO is harder to process than straight-run VGO and FCC cycle oils, because although DAO no longer contains asphaltenes, it still has a very high endpoint.

In traditional propane deasphalting, residual oil and propane are pumped to an extraction tower at 150–250 °F (65–120 °C) and 350–600 psig (2,514–4,240 kPa). Separation occurs in a tower, which may include a rotating disc

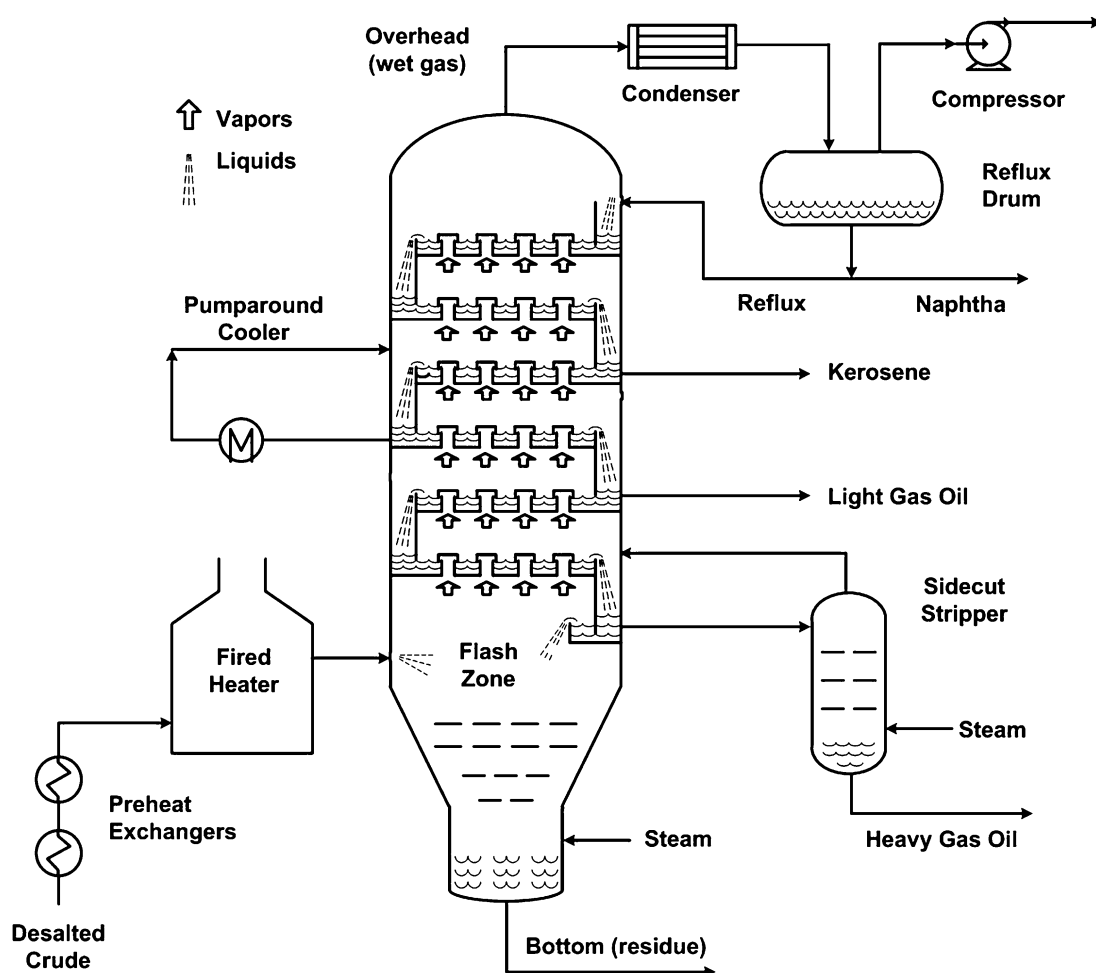


Fig. 18.28 Atmospheric distillation with bubble-cap trays [8], Fig. 10, with kind permission from Springer Science+Business Media, Inc

Table 18.12 Destinations for straight-run distillates

	Approx. boiling range fraction		Next destination	Ultimate product(s) or subsequent destination
	°C	°F		
LPG	−40 to 0	−40 to 31	Sweetener	Propane fuel
Light naphtha	39–85	80–185	Hydrotreater	Gasoline
Heavy naphtha	85–200	185–390	Cat. Reformer	Gasoline, aromatics
Kerosene	170–270	340–515	Hydrotreater	Jet fuel, No. 1 diesel
Gas oil	180–340	350–650	Hydrotreater	Heating Oil, No. 2 diesel
Atmos. resid	340+	650+	Visbreaker Resid hydrotreater Ebullated-bed hydrocracker	FCC or hydrocracker feed, low-viscosity resid Resid FCC Naphtha, gas oils, FCC
Vacuum gas oil	340–566	650–1,050	FCC Hydrotreater Hydrocracker Solvent refining	Gasoline, LCO, gases including C ₃ /C ₄ olefins Fuel oil, FCC, lubes Naphtha, jet, diesel, FCC, olefins, lubes DAO, asphalt
Vacuum Resid	+540	+1,000	Coker Solvent refining Slurry-phase hydrocracker	Coke, coker gas oil, coker naphtha, gases DAO, asphalt Traditional hydrotreater or hydrocracker

Resid is an abbreviation for residue, and 340+ (etc.) means everything that boils above 340 °C (etc.)

contactor. Liquid products are evaporated and steam stripped to recover the propane solvent, which is recycled.

An advanced version of solvent deasphalting is “residue oil supercritical extraction,” or ROSE. The ROSE™ Process was developed by the Kerr-McGee Corporation and now is offered for license by KBR. In this process, residue and solvent are mixed and heated to above the critical temperature of the solvent. Liquid yields are higher under supercritical conditions, because the lighter part of the oil becomes more soluble. In addition to giving higher yields, the process is more energy efficient and has lower operating costs due to improved solvent recovery. The ROSE process can employ three different solvents, the choice of which depends upon process objectives:

Propane	Preparation of lube base stocks
Butane	Asphalt production
Pentane	Maximum recovery of liquid

Solvent extraction is used to remove aromatics and other impurities from lube base stocks and grease stocks. The feedstock is dried, then contacted with the solvent in a counter-current or rotating disk extraction unit. The solvent is separated from the product stream by heating, evaporation, or fractionation. Remaining traces of solvent are removed from the raffinate by steam stripping or flashing. Electrostatic precipitators can enhance separation of inorganic compounds. The solvent is then regenerated and recycled. Today, phenol, furfural, and cresylic acid are widely used as solvents. Liquid sulfur dioxide, chlorinated ethers, and nitrobenzene also have been used.

Solvent dewaxing removes wax (normal paraffins) from deasphalted lube base stocks. The main process steps include mixing the feedstock with the solvent, chilling the mixture to crystallize wax, and recovering the solvent. Commonly used solvents include toluene and methyl ethyl ketone (MEK). Methyl-isobutyl ketone (MIBK) is used in a *wax deoiling* process to prepare food-grade wax, which is used to coat the paper used for milk cartons and other such products.

Visbreaking. Visbreaking is a mild form of thermal cracking that achieves about 15 % conversion of atmospheric residue into gas oils and naphtha. At the same time, a low-viscosity residual fuel is produced. The two main types of visbreaking are “short-contact” and “soaker.” In short-contact visbreaking, the feed is heated to about 900 °F (480 °C) and sent to a soaking zone reactor at 140–300 psig (1,067–2,170 kPa). The elevated pressure allows cracking to occur while restricting coke formation. To avoid over-cracking, the residence time in the soaking zone is short—several minutes compared to several hours in a delayed coker. The hot oil is quenched with cold gas oil to inhibit further cracking and sent to a vacuum tower for product

separation. Soaker visbreaking keeps the hot oil at elevated temperature for a longer time to increase the yield of middle distillates. Low-viscosity visbreaker gas oil can be sent to an FCC unit or hydrocracker for further processing, or used as heavy fuel oil.

Delayed coking. Delayed coking is a cyclic process that employs several coke drums. The drums operate on staggered 18 to 24-h cycles. Each cycle includes preheating the drum, filling it with hot oil, allowing coke and liquid products to form, cooling the drum, and decoking. As it is pumped into a drum, vacuum residue feed is heated to about 900–970 °F (487–520 °C). Thermal cracking begins immediately, generating coke and cracked products. Coke accumulates in the drum while the vapors go to a product fractionator. Meanwhile, hot feed keeps flowing into the drum until it is filled with solid coke. At the end of a cycle, the top and bottom heads of the drum are removed. A rotating cutting tool uses high-pressure jets of water to drill a hole through the center of the coke from top to bottom. In addition to cutting the hole, the water also cools the coke, forming steam as it does so. The cutter is then raised, step by step, cutting the coke into lumps, which fall out the bottom of the drum.

Light products include coker naphtha, light coker gas oil (LCGO), and heavy coker gas oil (HCGO). All of these require further processing due to their high content of olefins, which makes them unstable and poorly suited for direct blending into finished products. The coker naphtha and LCGO are hydrotreated. The HCGO can go either to an FCC unit or a hydrocracker.

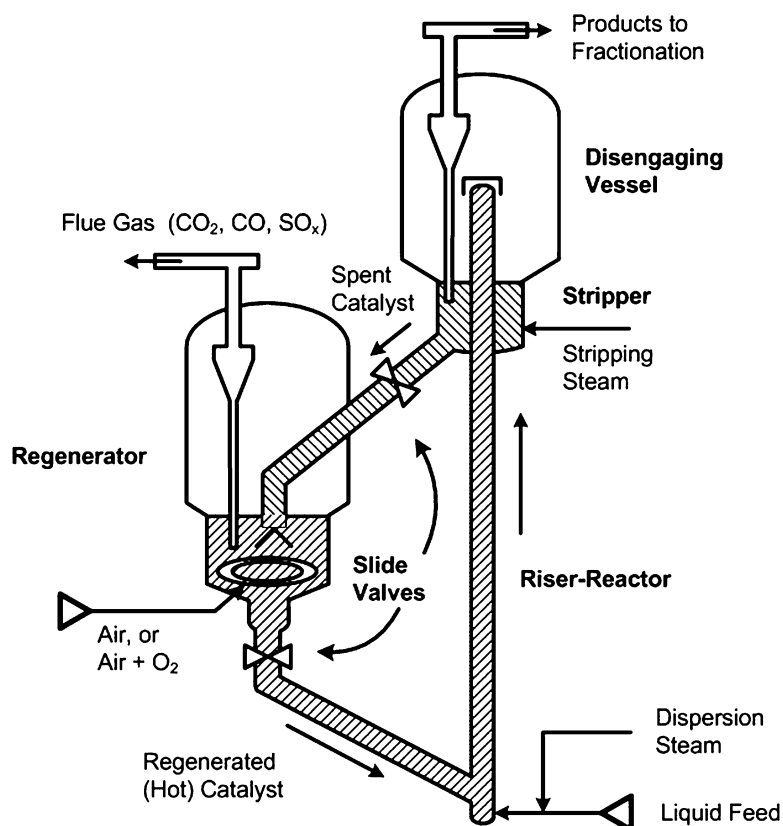
Coke can account for up to 30 wt.% of the product. It can be shipped by rail, truck, or conveyor belt to a calciner, which converts *green coke* fresh from the unit into various grades of petroleum coke. Green coke can also be used as-is for fuel.

Sponge coke is named for its sponge-like appearance. It is produced from feeds that have low-to-moderate asphaltene concentrations. If sponge coke meets certain specifications, it can be used to make carbon anodes for the aluminum industry. Otherwise, it serves as a fuel. Sponge coke must be calcined before it can be formed into anodes. Fuel coke sometimes is used without prior calcination.

Needle coke, named for its needle-like structure, is a high-value product made from feeds that contain nil asphaltenes, such as hydrotreated FCC decant oils. Needle coke is converted into graphite electrodes for the electric-arc furnaces used in the steel industry.

Shot coke is undesirable because it tends to be unstable. It forms when the concentration of feedstock asphaltenes and/or coke-drum temperatures are too high. A block of shot coke is a cluster of discrete mini-balls 0.1–0.2 in. (2–5 mm) in diameter. The clusters can be as large as

Fig. 18.29 FCC process flow [8], Fig. 13, with kind permission from Springer Science+Business Media, Inc



10 in. (25 cm) across. If a cluster breaks apart when the coke drum is opened, it can spray a volley of hot mini-balls in every direction. Adding aromatic feeds, such as FCC decant oil, can eliminate shot coke formation. Other methods of eliminating shot coke—decreasing temperature, increasing drum pressure, increasing the amount of product recycle—decrease liquid yields, which is not desired.

Specialty carbon products made from petroleum include recarburizer coke, which is used to make special steels, and titanium dioxide coke, which is used as a reducing agent in the titanium dioxide pigment industry.

Fluid coking. Fluid coking, also called continuous coking, is a moving-bed process for which the operating temperature is higher than the temperatures used for delayed coking. In continuous coking, hot recycled coke particles are combined with liquid feed in a radial reactor at about 50 psig (446 kPa). Vapors are taken from the reactor, quenched to stop any further reaction, and fractionated. The coke goes to a surge drum, then to a classifier, where the larger particles are removed as product. The smaller coke particles are recycled to a preheater, where they are mixed with fresh feed. Coking occurs both in the reactor and in the surge drum. Installation costs for fluid coking are somewhat higher than for delayed coking, but feeds can be heavier and heat losses are lower. Fluid coking makes more fuel gas than delayed coking.

Fluid catalytic cracking (FCC). FCC produces more than half the world's gasoline.

FCC process flow. A typical FCC unit (Fig. 18.29) comprises three major sections—riser/reactor, regenerator, and fractionation. In the riser/reaction section, preheated oil is mixed with hot, regenerated catalyst. The mixture acts as a fluid because the catalyst particles are about the size of sifted flour. The hot catalyst vaporizes the oil, and the vaporized oil carries the catalyst up the riser/reactor. The cracking reaction is very fast. It produces light gases, high-octane gasoline, and heavier products called light cycle oil (LCO), heavy cycle oil (HCO), slurry oil, and decant oil. It also leaves a layer of coke on the catalyst particles, rendering them inactive.

At the top of the riser, the riser outlet temperature (ROT) can reach 900–1,020 °F (482–549 °C). The ROT determines conversion and affects product selectivity, so FCC operators control it as tightly as possible. Higher temperatures favor production of olefin-rich light gases, especially propylene, at the expense of gasoline; many FCC units maximize propylene for use in nearby olefin plants. Moderate temperatures favor gasoline production. Lower temperatures decrease gasoline yields and increase heavier products—LCO and HCO.

In the disengaging section, steam helps separate the now-deactivated catalyst from the reaction products. The catalyst goes to the regenerator, where the coke is burned away by

fluidized combustion in the presence of air or oxygen-enriched air. The regenerated catalyst is hot, with temperatures up to 1,350 °F (732 °C). It is returned to the riser/reactor, where the cycle begins again.

In a 60,000 barrels-per-day unit processing a typical mixture of vacuum gas oils, the total catalyst in the unit (the “inventory”) is 400–500 tons. To maintain activity, about 0.5–1 wt.% of the inventory is replaced each day. If the feed to the unit contains significant amounts of residue, the replacement rate is higher. The discharged catalyst is cooled and shipped either to a land fill for disposal or to another refiner, which may have a particular use for “conditioned” FCC catalyst.

FCC feed pretreating. These days, most refiners pretreat FCC feeds in a fixed-bed hydrotreater. The hydrotreater removes trace metal contaminants such as nickel and vanadium. Nickel increases coke formation and decreases liquid yields. Vanadium reduces conversion, decreases liquid yields, and destroys the catalyst. In addition to removing Ni and V, the pretreater decreases concentrations of sulfur, nitrogen, and aromatics. In the FCC regenerator, sulfur on the coked catalyst is converted to sulfur oxides (SO_x) in the flue gas. Clean air regulations restrict SO_x emissions, which cause acid rain. Therefore, removing sulfur from the FCC feed—thereby reducing SO_x formation—is highly beneficial. Removing nitrogen is beneficial, too, because basic feed nitrogen suppresses the activity of highly acidic FCC catalysts. Pretreating also saturates aromatics. As we have seen, saturating aromatics makes them more crackable, so pretreating increases FCC conversion, often by more than 10 vol.%.

FCC heat balance. FCC units must be heat-balanced, or they won’t run. The burning of coke in the regenerator provides all of the heat required by the process. In fact, FCC units are significant sources of high-quality steam for other refinery units. Table 18.13 gives a representative breakdown of FCC heat requirements.

Residue FCC. Some FCC units process significant amounts of residue. These units use catalyst coolers (e.g., steam coils) in the regenerator or a second regeneration zone to remove excess heat from the unit. This is because residue generates substantially more coke than conventional FCC feeds, and excess heat is generated when the extra coke is burned off the catalyst. The trace-metal content of residues can be very high. Trace metals destroy FCC catalysts, so removing them—usually with hydrotreating—is essential.

Hydroprocessing. Hydrotreating and hydrocracking are similar processes. Their flow schemes are similar. Both use high-pressure hydrogen to catalytically remove

Table 18.13 Representative FCC heat balance

Factor	Portion of total
Heat up and vaporize fresh feed	40–50 %
Heat recycled oil	0–10 %
Heat of reaction (endothermic)	15–30 %
Heat steam	2–8 %
Heat losses	2–5 %
Heat air to regenerator temperature	15–25 %
Heat coke from the reactor to regenerator temperature	1–2 %
Total heat duty	500–1,000 Btu/lb 1160–2,325 kJ/kg

contaminants from petroleum fractions. Both employ the same kinds of equipment—pumps, compressors, furnaces, heat exchangers, and product recovery hardware. In most cases, fixed-bed hot-wall reactors are used. Feeds and products for typical hydrotreaters and hydrocrackers are shown in Table 18.14.

Hydrotreating. Hydrotreating is used to convert sulfur-containing hydrocarbons into low-sulfur liquids and hydrogen sulfide. It also removes nitrogen, oxygen, and other trace contaminants. Hydrotreater feeds range from naphtha to vacuum residues. Generally, each fraction is treated separately. Materials with higher boiling points require more severe treatment conditions. For example, naphtha hydrotreating can be done at 200–500 psia and at 500–650 °F with a hydrogen consumption of 10–50 scf/bbl of feed. Conversely, a residue hydrotreating process might operate at 2,000 psia and at 650–800 °F, with a hydrogen consumption of 600–1,200 scf/bbl.

Figure 18.30 presents a process flow scheme for a two-reactor fixed-bed hydrotreater. Units designed for light feeds usually are simpler, with only one reactor and sometimes only one catalyst bed. Reaction conditions depend on feed quality and process objectives. Oil and hydrogen-rich gas flow down through reactors loaded with catalysts. Makeup gas comes in to replace consumed hydrogen. Gas flow can be once-through in naphtha hydrotreaters, but in distillate and VGO hydrotreaters, unconsumed hydrogen is recycled.

Hydrotreating produces both H₂S and NH₃. Under reaction conditions, these remain in the gas phase. But at lower temperatures, they combine to form solid ammonium bisulfide (NH₄SH). Ammonia also reacts with chlorides to form NH₄Cl; chloride can come with makeup gas, feed, or wash water. These salts can deposit in air coolers and heat exchangers, blocking flow and—even worse—inducing corrosion. Fortunately, they are water-soluble, so they can be controlled by injecting wash water into the reactor effluent.

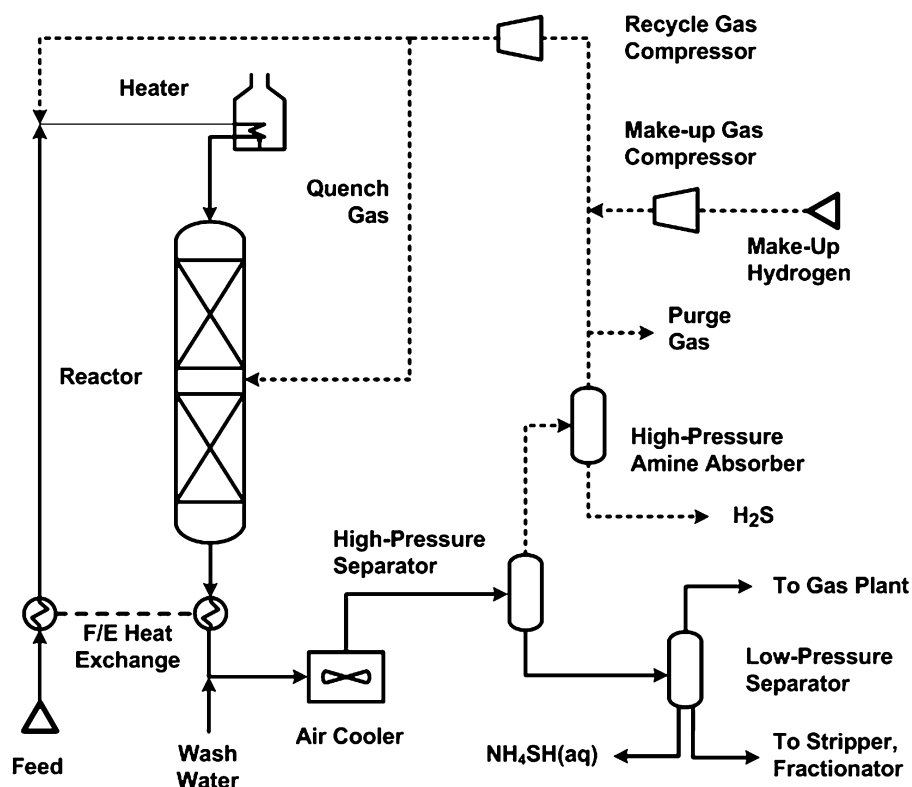
FCC gasoline post-treating. Conventional hydrotreating does a good job of removing sulfur from FCC gasoline.

Table 18.14 Feeds and products for hydroprocessing units

Feeds	Products from hydrotreating	Products from hydrocracking
Naphtha	Catalytic reformer feed	LPG
Straight-run light gas oil	Kerosene, jet fuel	Naphtha
Straight-run heavy gas oil	Diesel fuel	Naphtha
Atmospheric residue	Lube base stock, low-sulfur fuel oil, RFCC ^a feed	Naphtha, middle distillates, FCC feed
Vacuum gas oil	FCC feed, lube base stock	Naphtha, middle distillates, FCC feed, lube base stock, C = plant feed
Vacuum residue	RFCC ^a feed	See note ^b
FCC light cycle oil	Diesel blend stocks, fuel oil	Naphtha
FCC heavy cycle oil	Blend stock for fuel oil	Naphtha, middle distillates
Visbreaker gas oil	Diesel blend stocks, fuel oil	Naphtha, middle distillates
Coker gas oil	FCC feed	Naphtha, middle distillates, FCC feed, lube base stock, C = plant feed
Deasphalted oil	Lube base stock, FCC feed	Naphtha, middle distillates, FCC feed, lube base stock

^aRFCC = “residue FCC unit” or “reduced crude FCC unit,” which are specially designed to process feeds that contain high concentrations carbon-forming compounds

^bTraditional fixed-bed hydrocrackers cannot process vacuum residue. However, ebullated-bed and slurry-phase hydrocrackers can. Products from the latter include naphtha, middle distillates, and FCC feed

**Fig. 18.30** Fixed-bed hydrotreating process flow [15], Fig. 10.20, with kind permission from Woodhead Publishing

Unfortunately, it also does a good job of reducing octane by saturating C_6 – C_{10} olefins. Several processes remove sulfur at minimum octane loss. Licensors include Axens (IFP), CDTECH, ExxonMobil, and UOP. The ConocoPhillips S Zorb process uses selective adsorption to remove sulfur from FCC gasoline. The feed is combined with a small amount of hydrogen, heated, and injected into an expanded

fluid-bed reactor, where a proprietary sorbent removes sulfur from the feed. A disengaging zone in the reactor removes suspended sorbent from the vapor, which exits the reactor as a low-sulfur stock suitable for gasoline blending. The sorbent is withdrawn continuously from the reactor and sent to the regenerator section, where the sulfur is removed as SO_2 and sent to a sulfur recovery unit. The clean sorbent is

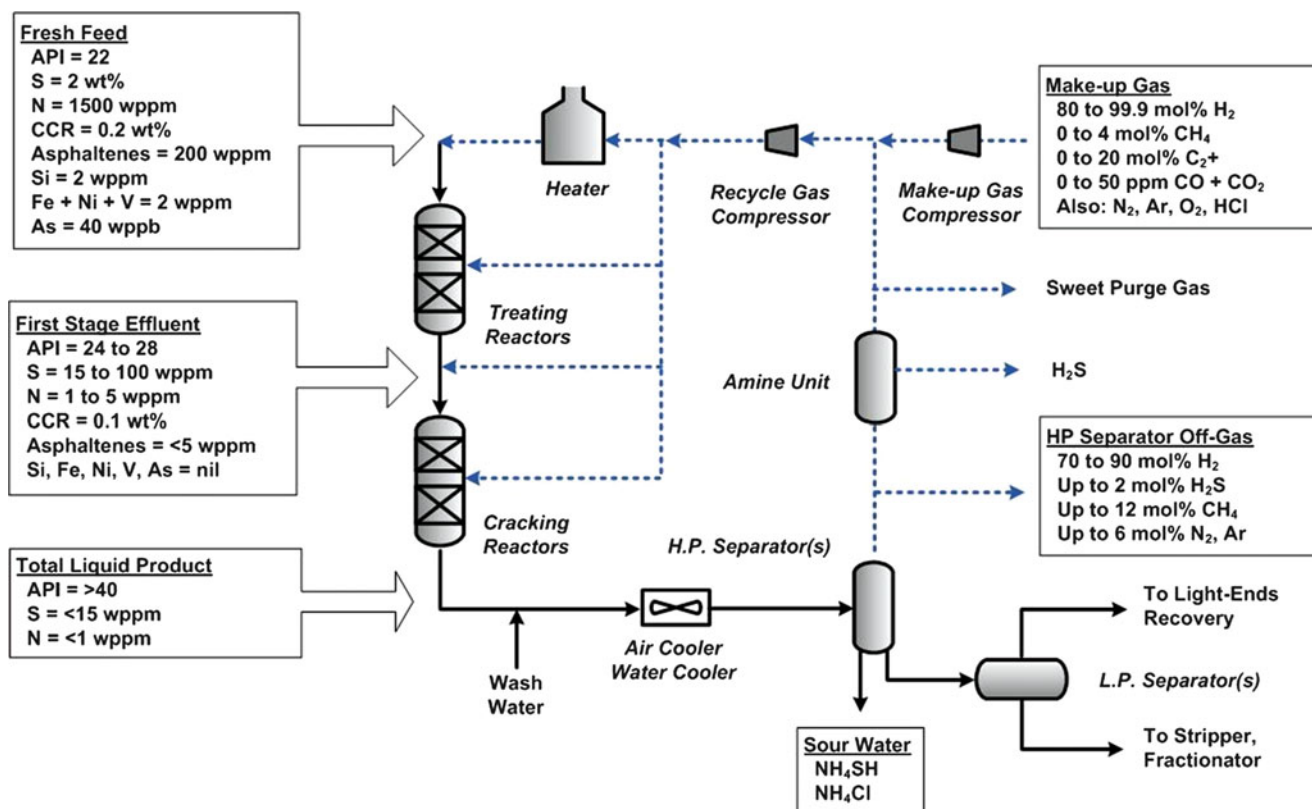


Fig. 18.31 Once-through hydrocracking process flow [15], Fig. 10.21, with kind permission from Woodhead Publishing

reconditioned and returned to the reactor. The rate of sorbent circulation is controlled to help maintain the desired sulfur concentration in the product.

Fixed-bed hydrocracking. As with other conversion processes, the purpose of hydrocracking is to break carbon–carbon bonds, thereby converting heavy hydrocarbons into lighter ones. Figure 18.31 shows a two-reactor once-through hydrocracker with some typical properties for feed and product streams. Figure 18.32 shows a two-stage hydrocracker, in which unconverted oil from the first two reactors goes to a third reactor for additional conversion. With respect to equipment and process flow, fixed-bed hydrocrackers are similar to fixed-bed hydrotreaters. Hydrotreating is an integral part of hydrocracking, because hydrotreating is used to remove organic nitrogen from the feed. Organic nitrogen poisons acidic cracking sites, so its removal is essential.

As shown in Table 18.15, a fixed-bed hydrocracking unit can have significant product flexibility, producing either large amounts of C₄-plus naphtha or large amounts of middle distillates. In petroleum refining, this kind of flexibility is unique.

Ebullated-bed hydrocracking. In contrast to fixed-bed hydrocrackers, ebullated-bed (e-bed) units can process large amounts of residual oils. Catalyst life does not limit

these units, because fresh catalyst is added and spent catalyst is removed continuously. In e-bed units (Fig. 18.33), hydrogen-rich recycle gas is bubbled up through a mixture of oil and catalyst particles. This provides three-phase turbulent mixing, which is needed to ensure a uniform temperature distribution. At the top of the reactor, catalyst is disengaged from the process fluids, which are separated in downstream flash drums. Most of the catalyst is returned to the reactor. Some is withdrawn and replaced with fresh catalyst. When compared to fixed-bed processes e-bed technology offers the following advantages:

- The ability to achieve more than 50 wt.% conversion of atmospheric residue
- Ample free space between catalyst particles, which allows entrained solids to pass through the reactor without accumulation, plugging, or build up of pressure drop
- Better liquid-product quality than delayed coking

Disadvantages versus fixed-bed processes include high catalyst attrition, which leads to high rates of catalyst consumption; higher installation costs due to larger reactor volume and higher operating temperatures; and sediment formation. Recent improvements include second-generation catalysts with lower attrition; catalyst rejuvenation, which allows the reuse of spent catalysts; improved reactor design leading to higher single-train feed rates; and two-reactor layouts with inter-stage separation.

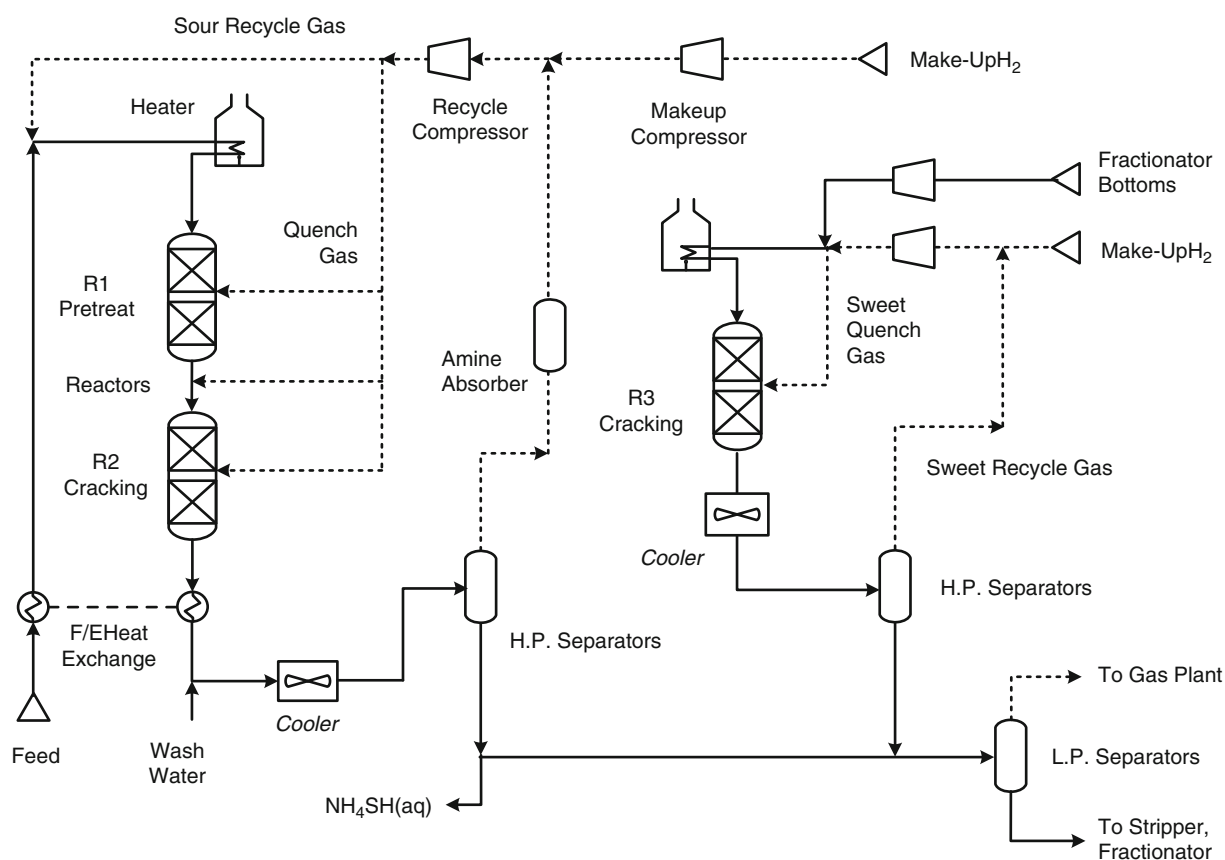


Fig. 18.32 Two-stage hydrocracking process flow [15], Fig. 10.22, with kind permission from Woodhead Publishing

Slurry-phase hydrocracking. Slurry-phase hydrocracking (Fig. 18.34) achieves 95 wt.% conversion of vacuum residue or coal tar. Process conditions are severe—more than 840 °F (450 °C) and 2,000–3,000 psig (14,000–20,800 kPa). The catalysts are nonacidic, comprising finely divided carbon or powdered iron sulfate. Inside the reactor, the liquid/powder mixture behaves as a single phase due to the small size of the additive particles. The additives prevent bulk coking by providing highly dispersed nucleation sites for “micro coking” per [26]. The additive isn’t recovered. Instead, it ends up in a pitch fraction, which comprises <5 wt.% of the vacuum residue or coal tar feed.

The advantages of slurry-phase processes include:

- The ability to achieve more than 95 wt.% conversion of vacuum residue and other feedstocks, including coal [33]
- Good product quality in two-stage designs, which incorporate a fixed-bed hydrotreating/hydrocracking reactor
- Feedstock flexibility
- Low-cost, micron-size disposable catalysts
- For a given volume of residue feed, lower reactor volume than e-bed processes

Disadvantages include the need to dispose of the coproduced pitch.

Catalytic reforming. The three major process flows for catalytic reforming are:

- Semi-regenerative
- Cyclic
- Continuous catalyst regeneration (CCR)

Figure 18.35 shows a fixed-bed semi-regen reformer. Catalyst cycles last from 6 to 12 months. A cycle ends when the unit is unable to meet its process objectives—typically octane and overall C₅-plus yields. At the end of a cycle, the entire unit is brought down and coke is burned off the catalyst. Desulfurized naphtha is mixed with hydrogen, heated to >900 °F (>480 °C) and passed through a series of fixed-bed reactors. At mentioned the feed is spiked with an organic chloride, which converts to hydrogen chloride in the reactors. This provides the required catalyst acidity and helps minimize catalyst coking.

The major chemical reactions—dehydrogenation and dehydrocyclization—are endothermic and the reactors are adiabatic. Consequently, the temperature drops as reactants flow through a reactor. Between reactors, fired heaters bring the process fluids back to desired reactor inlet temperatures (RIT). The last reactor effluent is cooled and sent to a separator, from which hydrogen-rich gas is removed and

Table 18.15 Hydrocracking product flexibility

Feed	Straight-run vacuum gas oil		
Boiling range, °C	340–550		
Boiling range, °F	644–1,020		
API gravity	22.0		
Specific gravity	0.9218		
Nitrogen, wppm	950		
Sulfur, wt%	2.5		
Primary product objective	Naphtha	Kerosene	Gas oil
Weighted average reactor temp, °C	base	–6	–12
Weighted average reactor temp, °F	base	–11	–22
Product yields, vol % fresh feed			
Butanes	11	8	7
Light naphtha	25	18	16
Heavy naphtha	90	29	21
Kerosene or gas oil	–	69	77
Total C ₄ -plus	126	124	121
Chemical H ₂ consumption			
Nm ³ /m ³	345	315	292
Scf/bbl	2,050	1,870	1,730
Product qualities			
Light naphtha (C ₅ –82 °C)			
RON Clear	79	79	80
Heavy naphtha			
P/N/A	45/50/5	44/52/4	–
RON clear	41	63	67
End point, °C (°F)	216 (421)	121 (250)	118 (244)
Kerosene			
Flash point, °C (°F)	–	38 (100)	–
Freeze point, °C (°F)	–	–48 (–54)	–
Smoke point, mm	–	34	–
FIA aromatics, vol%	–	7	–
End point, °C (°F)	–	282 (540)	–
Gas oil			
Cloud point, °C (°F)	–	–	–15 (5)
API gravity	–	–	44
Cetane number	–	–	55
Flash point, °C (°F)	–	–	52 (126)
End point, °C (°F)	–	–	349 (660)

recycled to the reactors. The liquid product flows to a stabilizer column, where entrained gases are removed, before going to the gasoline blender or aromatics plant.

A cyclic reformer has more reactors, and catalyst cycles are shorter—20 to 40 h. Shutdowns are staggered so that only one reactor is down at a given time.

In the CCR Platforming process (Fig. 18.36) hydrotreated feed mixes with recycle hydrogen and goes to a series of adiabatic, radial-flow reactors arranged in a vertical stack. Catalyst flows down the stack, while the reaction fluids flow radially through the catalyst beds. Heaters are used between reactors to reheat the reaction fluids to the required temperature. Flue gas from the fired heaters is typically used to generate steam. A CCR can operate at very low pressure (100 psig, 791 kPa). This improves yields of aromatics and hydrogen, but it accelerates catalyst deactivation by increasing the rate of coke formation. But faster coke formation is

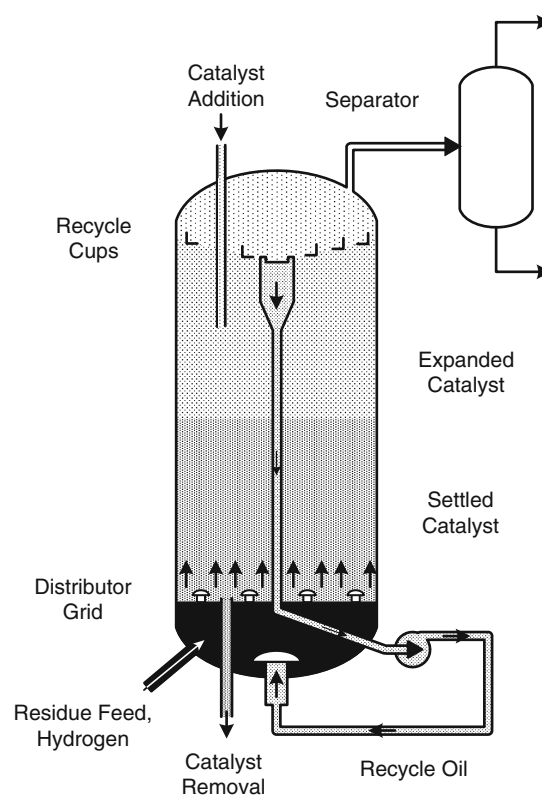


Fig. 18.33 Ebullated-bed hydrocracking process flow [32], Fig. 21, with kind permission from Springer Science+Business Media, Inc

okay in a CCR reformer, because the catalyst always is being regenerated.

Isomerization. As mentioned, isomerization units convert *n*-paraffins into isoparaffins and straight-chain olefins into iso-olefins. Butane isomerization provides isobutane for subsequent alkylation. Pentane/hexane isomerization improves the octane of light naphtha streams.

In butane isomerization, the feed contains *n*-butane or, more typically, mixed butanes. The catalyst is highly sensitive to water, so the feed must be thoroughly dried. In the low-temperature first stage, the catalyst comprises aluminum chloride promoted by HCl. Hydrogen gas is added to inhibit olefin formation. In the high-temperature second stage, the catalyst contains a noble metal such as platinum. Temperatures range from 230 to 340 °F (110–170 °C) and pressure ranges from 200 to 300 psi (14–20 bar). The reactor effluent goes to a flash drum, from which hydrogen is recovered and recycled. HCl is removed in a stripper column. The liquids go to a fractionator (deisobutanizer), which separates unconverted *n*-butane from the isobutane product. The *n*-butane is mixed with fresh feed and recycled.

In the Shell Hysomer process for pentane/hexane isomerization, the feed is combined with hydrogen-rich gas, heated to 445–545 °F (230–285 °C) and routed to the

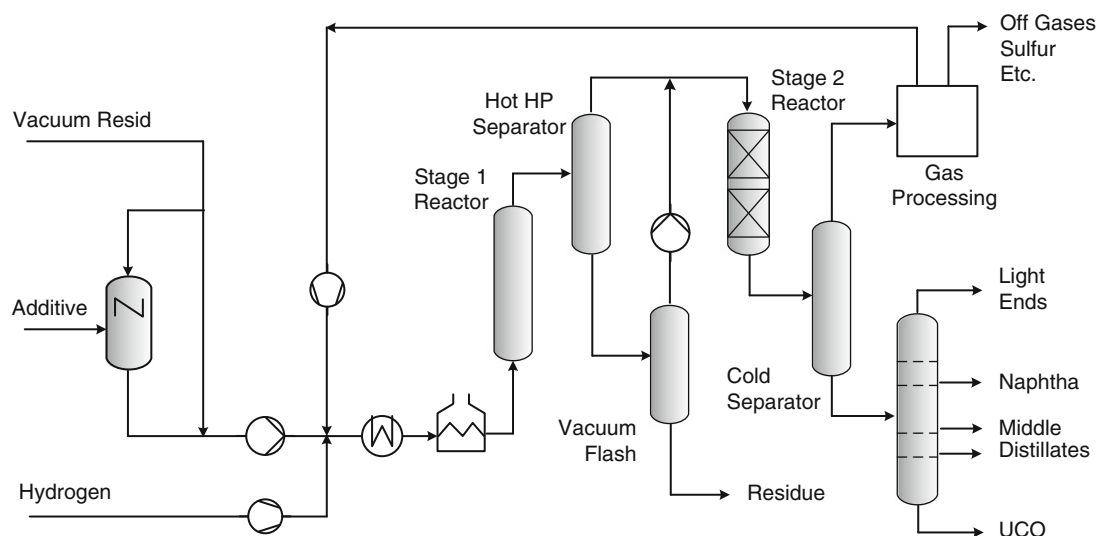


Fig. 18.34 Two-stage slurry-phase hydrocracking process flow. Based on drawings supplied by KBR Technology. Used with kind permission from KBR, Inc

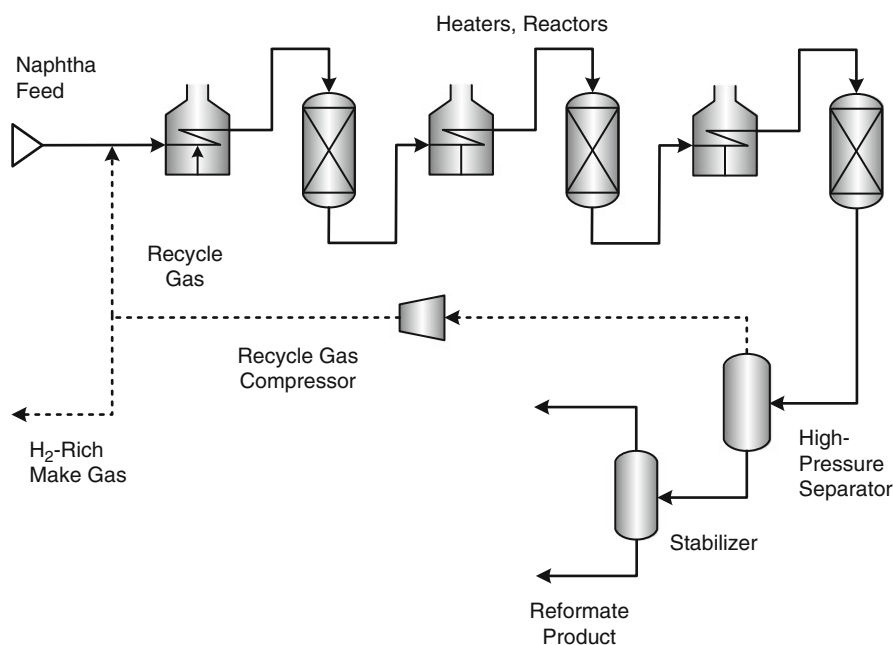


Fig. 18.35 Semi-regen catalytic reforming process flow [8], Fig. 18, with permission from Springer Science+Business Media, Inc

Hysomer reactor at 190–440 psi (13–30 bar). As with fixed-bed hydrotreating and hydrocracking, the process fluids flow down through the catalyst bed, where a part of the *n*-paraffins are converted into branched paraffins. The catalyst is comprised of a noble metal on a zeolite-containing support. The reactions are exothermic, and temperature rise is controlled by injecting relatively cold quench gas. The reactor effluent is cooled and sent to a flash drum, which separates hydrogen from the liquid product. The hydrogen is recycled. The liquid is

fractionated, and the *n*-paraffins are recycled. The net conversion of *n*-paraffins into branched products can be as high as 97 %, and the octane can be boosted by 8–10 numbers.

Often, the heat-exchanger and fractionation systems of isomerization units are integrated with those of other process units, such as catalytic reformers. In the total isomerization process (TIP), C5/C6 isomerization is integrated with molecular sieve separation, which provides complete conversion to *n*-paraffins.

The diagram illustrates a hydrotreating process. It features a Regenerator, a set of Reactors, and a Heater. Hydrotreated Feed enters from the bottom and is pumped into the Reactors. The effluent from the Reactors goes to a Separator. The Separator produces Liquid Products and a gas stream. The gas stream is further processed to yield H2-Rich Net Gas and Recycle Gas. The Recycle Gas is fed back into the Reactors. The Regenerator is used for catalyst regeneration, with a dashed line indicating a cycle between the Reactors and the Regenerator.

The diagram illustrates the process flow for HF-catalyzed isomerization. Feedstocks 'Olefins, Isobutane' enter a 'Reactor' at the top left. 'Fresh Acid' is added to the reactor. The reactor effluent goes to a 'Settler'. The bottom product of the settler is 'HF', which is sent to an 'HF Regenerator'. The top product of the regenerator is 'Acid Oils'. The bottom product of the regenerator goes to a 'Deisobutanizer'. The top product of the deisobutanizer is 'HF Recycle', which is sent back to the reactor. The bottom product of the deisobutanizer goes to an 'Acid Stripper'. The top product of the acid stripper is 'Fresh Acid', which is sent back to the reactor. The bottom product of the acid stripper goes to a 'Depropanizer'. The top product of the depropanizer is 'Propane'. The bottom product of the depropanizer goes to a 'Debutanizer'. The top product of the debutanizer is 'N-Butane'. The bottom product of the debutanizer is 'Alkylate'. The bottom product of the depropanizer also goes to a 'Defluorinator', which has an outlet at the bottom.

Related materials are used in other processes. For example, metal-promoted silica-alumina phosphates such as SAPO-11 are used to isomerize normal paraffins in catalytic dewaxing (CDW) units.

Figure 18.38 shows six zeolite structures. In cracking catalysts, HY zeolite is the most common, but beta and ZSM-5 are used as well. The building blocks of A, X, and other zeolites are tetrahedral units of Si and Al oxides. In the ultra-stable Y (USY) zeolites employed in cracking catalysts, the Si/Al ratio is >10 .

Most of the processes we have discussed require catalysts. Except for alkylation units, where the acids are in liquid

Fig. 18.38 Structures of zeolites ZSM-5 (a), mordenite (b), beta (c), MCM-22 (d), zeolite Y (e), and zeolite L (f). This image is Fig. 1 in [34]

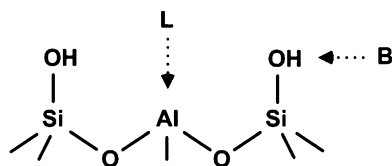
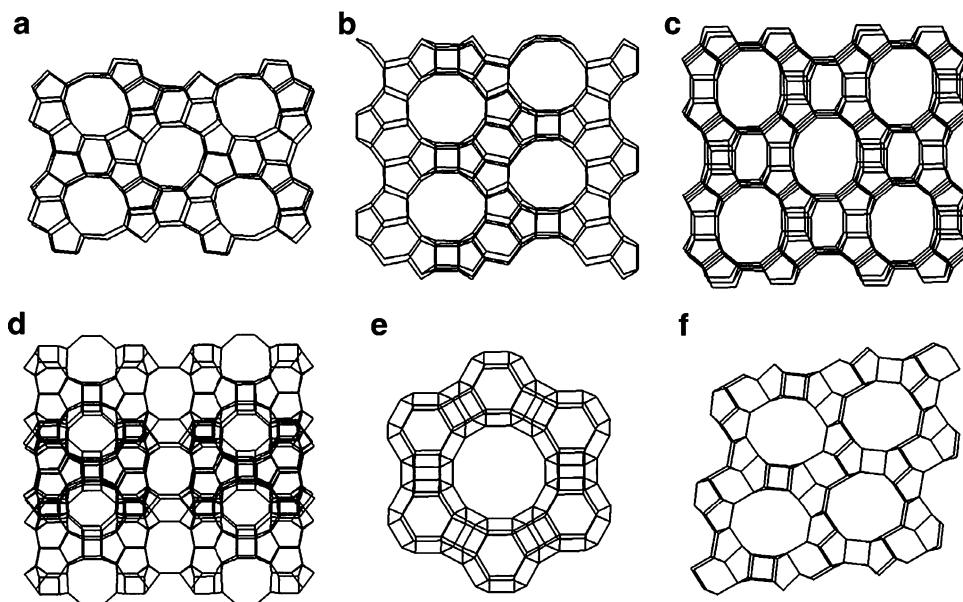


Fig. 18.39 Brønsted (B) and Lewis acid sites (L) in zeolites. Adapted from Fig. 6 in [35]

The acidity of zeolites comes from their structure. Figure 18.39 shows how one can picture these materials as a silica (SiO_2) superstructure, in which every so often an aluminum atom replaces a silicon atom. The silicon atoms have a valence of +4, and each one binds to four oxygen atoms. The oxygen atoms in hydroxyl groups are Brønsted acids (proton donors). Replacing Si (+4) with Al (+3) creates electron-rich Lewis acid sites, which are associated with positive counter-ion such as Na^+ , K^+ , NH_4^+ , or H^+ . The counter ions can be swapped via ion exchange. For example, when Na-Y zeolite is exchanged with an ammonium salt, the Na^+ ion is replaced by NH_4^+ . When NH_4 -Y is heated to the right temperature, the ammonium ion decomposes, releasing NH_3 (gas) and leaving behind highly acid HY zeolite.

ZSM-5 is a shape-selective zeolite made by including a soluble organic template in the mix of raw materials. (Templates for this kind of synthesis include quarternary ammonium salts.) ZSM-5 enhances distillate yields in FCC units and CDW in hydroprocessing units, where due to its unique pore structure, it selectively cracks waxy n-paraffins into lighter molecules.

Amorphous silica-alumina (ASA) catalysts are also used for hydrocracking. ASA catalysts are less active but better for producing middle distillates. Figure 18.40 provides a

conceptual comparison of amorphous ASA catalysts with crystalline zeolite catalysts. The pore diameters of HY zeolite catalysts are uniform and relatively small—around 7.5 Ångstroms, give or take. Mesopores have larger diameters, which admit mid-sized molecules such as those found in vacuum gas oils. ASA catalysts include small, medium, and large pores. The width of ASA pores can exceed 100 Å. The larger pores can accommodate larger molecules, which explains why ASA catalysts do a better job of cracking feeds with very high endpoints. The pore diameter for ZSM-5 is 6.3 Å.

Catalyst Manufacturing

The following steps are used to prepare solid refinery catalysts:

- Precipitation
- Filtration (or centrifugation), washing, and drying
- Forming
- Calcining
- Impregnation and/or co-mulling
- Activation

Other steps, such as kneading, mulling, grinding, and/or sieving also may be used.

In the precipitation step, two solutions are combined to form a desired solid. For example, mixing a solution of aluminum nitrate [$\text{Al}(\text{NO}_3)_3$] with a solution of sodium aluminate [$\text{Na}_2\text{Al}_2\text{O}_4$] yields a gel of aluminum hydroxide [$\text{Al}(\text{OH})_3$]. As the gel ages, tiny crystals grow larger and a pore structure starts to develop.

Filtration, washing, and drying remove salts and other impurities. In our example, after the precipitation of Al

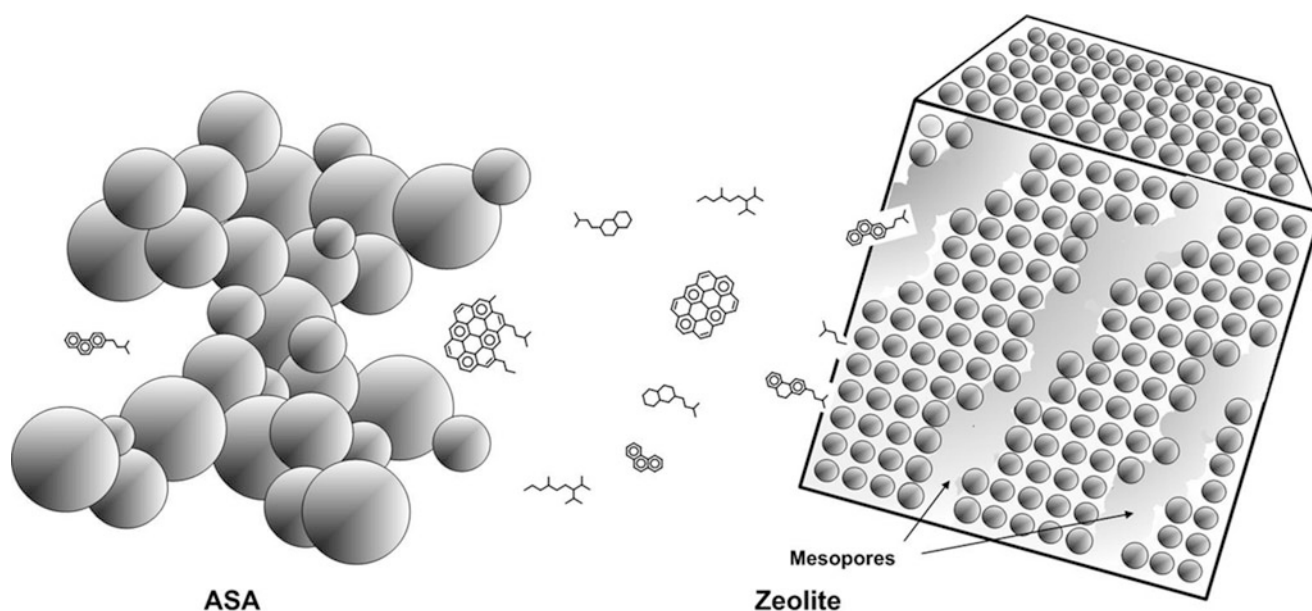


Fig. 18.40 Comparison of amorphous alumina silica (ASA) and zeolite cracking catalyst structures

(OH)₃ from aluminum nitrate and sodium aluminate, the coproduced sodium nitrate is washed away with water. Adding ammonium hydroxide expedites sodium removal. Subsequent drying removes excess water and initiates the transformation of Al(OH)₃ into alumina [Al₂O₃].

Catalysts can be shaped like wagon wheels, spheres, cylinders, hollow cylinders, lobed extrudates, pellets, etc. (Fig. 18.41). A cross-section of a lobed extrudate can look like a 3-leaf or 4-leaf clover without the stem. Compared to cylindrical extrudates, shaped extrudates have a higher surface-to-volume ratio, and the average distance from the outside of a particle to the center is shorter. To make extrudates, a paste is formed and forced through a die. The resulting spaghetti-like strands are dried and broken into short pieces with a length/diameter ratio of 2:4; for main-bed hydrotreating catalysts, diameters range from 1.3 to 4.8 mm. The particles are calcined, which hardens them and removes additional water and volatile molecules such as ammonia.

Spherical catalysts are made by (a) spray-drying slurries of catalyst precursors, (b) spraying liquid onto powders in a tilted rotating pan, or (c) dripping a silica-alumina slurry into hot oil. Pellets are made by compressing powders in a dye. FCC catalysts are made by spray drying.

Impregnation distributes active metals within the pores of a catalyst support. Like sponges, calcined supports are especially porous. Far more than 99 % of the surface area is inside the pores. When the pores are exposed to aqueous solutions containing active metals, capillary action pulls the aqueous phase into them. After drying, the catalyst might be soaked in another solution to increase the loading

of the same (or a different) active metal. Catalysts can also be made by co-mulling active metal oxides with the support. Co-mulling tends to cost less because it requires fewer steps. It also produces materials with different activities—sometimes higher, sometimes lower—than impregnation.

Catalyst Deactivation

Over time, refinery catalysts deactivate and must be replaced. The major causes of deactivation are feed contaminants (trace metals, particulates, etc.) and catalyst coking; the latter is discussed above in some detail. In FCC, continuous catalyst replacement (CCR) processes, and ebullated-bed hydrocracking, aged catalysts are continuously removed and replaced with fresh. But in fixed-bed units, catalyst replacement requires a shutdown. Large hydrocrackers can process >40,000 barrels of feed per day. With a typical net margin of \$15–20 per barrel for hydrocracking alone, every day of down time costs \$600,000 to \$800,000. When the hydrocracker comes down, refiners may have to shut down (or reduce feed rates in) other units, such as the catalytic reformer, which gets feed from the hydrocracker (see Fig. 18.13). Therefore, the refinery-wide cost of hydrocracker down time can be far greater than \$1 million per day.

For a fixed-bed hydrotreating or hydrocracking unit, catalyst cycles range from 12 to 36 months. At the start of a cycle, average reactor temperatures are low, ranging from 550 to 660 °F (288–349 °C). As the cycle proceeds, the catalyst deactivates, so operators must raise temperatures



Fig. 18.41 Catalyst loading scheme showing size/shape grading. Photo provided by Criterion Catalysts & Technologies, LLP

to maintain HDS, HDN, or conversion. A catalyst cycle ends for one of the following reasons:

- The temperature required to achieve the unit's main process objectives hits a metallurgical limit
- The main process objective can be met only at reduced feed rate
- Pressure drop across the unit reaches the upper limit
- Selectivity decreases. If the production of light gases exceeds the capacity of one or more towers in the downstream gas plant, operators must decrease feed rate or reduce conversion. Both options are expensive
- Feed upsets. For a fixed-bed hydrotreater, a slug of residue can poison part of the catalyst with trace contaminants or foul it with particulates, asphaltenes and/or refractory carbon
- Equipment failure. Hardware problems occur most frequently in rotating equipment—pumps and compressors

Petroleum Products

Product Specifications

Products from modern refineries comprise several individual streams, which are blended to meet desired specifications. Product specifications developed by ASTM International are widely used throughout the world. (Until 2001, ASTM was an acronym for the American Society for Testing and Materials.) Table 18.16 lists some common refinery products along with their ASTM designations.

Analogous institutions in other countries, such as British Standards Institution (BSI), serve similar functions. In addition to setting specifications, these institutions develop and publish test methods used to analyze a wide variety of materials. ASTM and its international cousins cooperate both with each other and with government regulators. For example, recent low-sulfur gasoline and diesel directives from the U.S. Environmental Protection Agency are incorporated into D975-04 and D4814-03a, respectively.

Other widely used tests and specifications are defined by licensors. For example, UOP's *Laboratory Test Methods*, distributed by ASTM, defines several hundred procedures for analyzing catalysts, chemicals, and fuels.

Additives are essential components of finished fuels. They increase stability, improve flow properties, and enhance performance. Cetane-improvers are routinely added to diesel fuel, and additives that prevent intake-valve

Table 18.16 ASTM specification numbers for hydrocarbon fuels

Product	ASTM specification	Description
Gasoline	D4814	Standard specification for automotive spark-ignition engine fuel
Jet	D1655	Standard specification for aviation turbine fuels
Kerosene	D3699	Standard specification for kerosene
Diesel	D975	Standard specification for diesel fuel oils
Fuel oil	D396	Standard specification for fuel oils

deposits are now required in all grades of gasoline in the United States.

Gasoline. In the mid- to late-twentieth Century, making gasoline was a relatively simple task. If a mixture of components met specifications for volatility and octane, it could be shipped to retail outlets and sold as-is. If the octane was low, the problem could be fixed by adding a little tetraethyl lead. Butanes could be added or left out as needed to adjust volatility. In 2010, due to environmental regulations, refiners must also meet restrictions on Reid Vapor Pressure (RVP), sulfur content, and oxygen content. Thanks to such restrictions, especially the limit on RVP, the air is much more breathable in large American and European cities.

Octane numbers for hydrocarbons. In a spark-ignition engine, some compounds start to burn before they reach the spark plug. This premature ignition causes knocking, which reduces the power of the engine, increases engine wear, and can cause serious damage. Octane number is a measure of the propensity of fuels to knock in gasoline engines. It is based on a scale in which the octane number of n-heptane is zero and the octane number of isooctane (2,2,4-trimethylpentane) is 100. When a fuel is tested in a standard single-cylinder engine, mixtures of isooctane and n-heptane are used as standards. ASTM D2699 and ASTM D2700 describe methods for measuring research octane number (RON) and motor octane number (MON), respectively.

In North America, the pump octane of gasoline is the average of RON and MON: $(R + M)/2$. This is the number displayed on pumps at filling stations. Typical grades are “regular” with a pump octane of 87, “mid-grade” with a pump octane of 89, and “premium” with a pump octane of 91–93. In some locales, customers can dial in any octane they want between 87 and 93.

Several refinery streams have the right vapor pressure, boiling range, sulfur content, and octane to end up in the gasoline pool. Table 18.17 shows properties for blend stocks from which gasoline might be made. The raffinate comes from an aromatics extraction unit, and the pyrolysis gasoline comes from a nearby ethylene plant.

Table 18.17 Gasoline blend stock composition and properties: examples

Component	Density (kg/m ³)	RVP (bar)	Boiling range		RON	MON
			°C	°F		
Butanes	0.575	3.6	−12 to −0.5	10.4–31	97	95
Straight-run Gasoline	0.64	1.15	27–80	81–176	80.2	76.6
Reformate	0.815	0.08	78–197	172–387	100.5	89.5
Raffinate	0.685	0.3	65–112	149–234	60.3	54.5
Heavy FCC Gasoline	0.76	0.2	43–185	109–365	90.5	79.5
Light FCC Gasoline	0.66	1.3	25–89	77–192	94.5	81.5
Pyrolysis gasoline	0.845	0.3	47–180	117–356	101.5	86.5
Alkylate	0.705	0.3	39–195	102–383	98	93.5
MTBE	0.746	0.5	48–62	118–144	115	97

Reformulated gasoline (RFG). In 1970, gasoline blending became more complex. The U.S. Clean Air Act required the phase-out of tetraethyl lead, so refiners had to find other ways to provide octane. In 1990, the Clean Air Act was amended. It empowered EPA to impose emissions limits on automobiles and to require reformulated gasoline (RFG). RFG was implemented in several phases. The Phase I program started in 1995 and mandated RFG for ten large metropolitan areas. Several other cities and four entire States joined the program voluntarily. In the year 2000, about 35 % of the gasoline in the United States was reformulated.

Tier 1 reformulated gasoline regulations required a minimum amount of chemically bound oxygen, imposed upper limits on benzene and RVP (RVP), and ordered a 15 % reduction in volatile organic compounds (VOC) and air toxics. VOC react with atmospheric NO_x to produce ground-level ozone. Air toxics include 1,3-butadiene, acetaldehyde, benzene, and formaldehyde.

The regulations for Tier 2, which took force in January 2000, were based on the EPA Complex Model, which estimates exhaust emissions for a region based on geography, time of year, mix of vehicle types, and—most important to refiners—fuel properties. As of 2006, the limit on sulfur in the gasoline produced by most refineries was 30 wppm.

Initially, the oxygen for RFG could be supplied as ethanol or C₅–C₇ ethers. The ethers have excellent blending octanes and low vapor pressures. But due to leaks from filling station storage tanks, methyl-t-butyl ether (MTBE) was detected in ground water samples in New York City, Lake Tahoe, and Santa Monica, California. In 1999, the Governor of California issued an executive order requiring the phase-out of MTBE as a gasoline component. That same year, the California Air Resources Board (CARB) adopted

Table 18.18 Additives used in gasoline

Additive type	Function
Oxygenates anti-oxidation	Decrease emissions Minimize oxidation and gum formation during storage
Metal passivation	Deactivate trace metals that can accelerate oxidation
Corrosion inhibition	Minimize rust throughout the gasoline supply chain
Anti-icing	Minimize ice in carburetors during cold weather
IVD control (detergent)	Control deposition of carbon on intake valves
CCD control	Control deposition of carbon in combustion chambers

California Phase 3 RFG standards, which took effect in stages starting in 2002. The standards include a ban on MTBE and a tighter cap on sulfur content—less than 15 wppm.

In many other countries, including Finland, MTBE is still considered a premium blend stock, as safe as other components when filling station storage tanks are properly maintained.

Gasoline additives. Table 18.18 lists the kinds of additives used to prepare finished gasoline. Additive packages vary from season-to-season, region-to-region, and retailer to retailer. After-market additives contain similar types of ingredients, and usually are more concentrated. They are packaged to be added by consumers to their own vehicles.

Low-sulfur gasoline and ultra-low-sulfur diesel. In recent years, the U.S. Environmental Protection Agency (EPA) and the European Parliament promulgated clean-fuel regulations that are lowering the sulfur content of gasoline and diesel fuel. New sulfur-content standards for on-road diesel fuel range from 10 wppm in EU countries to 15 wppm in the United States.

Diesel fuel. The most important property of diesel fuel is cetane number, which indicates how the fuel will perform in diesel engines. Other important diesel-fuel properties include flash point, cloud point, pour point, kinematic viscosity, lubricity—and of course sulfur. Cloud point and pour point indicate the temperature at which the fuel tends to thicken and then gel in cold weather. Viscosity measures the tendency of a fluid to flow. In a diesel engine, viscosity indicates how well a fuel atomizes in spray injectors. It also measures its quality as a lubricant for the fuel system. Lubricity measures the fuel's ability to reduce friction between solid surfaces in relative motion. It indicates how the engine will perform when loaded. Table 18.19 lists cetane numbers for selected pure compounds. As with

Table 18.19 Cetane numbers for selected pure compounds

Compound	Type	Carbons	Formula	Cetane No.
n-Decane	Paraffin	10	C ₁₀ H ₂₂	76
Decalin	Naphthene	10	C ₁₀ H ₁₈	48
α-Methylnaphthalene	Aromatic	11	C ₁₁ H ₁₀	0 ^a
n-Pentylbenzene	Aromatic	11	C ₁₁ H ₁₆	8
3-Ethyldecane	Paraffin (iso)	12	C ₁₂ H ₂₆	48
4,5-Diethyloctane	Paraffin (iso)	12	C ₁₂ H ₂₆	20
3-Cyclohexylhexane	Naphthene	12	C ₁₂ H ₂₄	36
Biphenyl	Aromatic	12	C ₁₂ H ₁₀	21
α-Butylnaphthalene	Aromatic	14	C ₁₄ H ₁₆	6
n-Pentadecane	Paraffin	15	C ₁₅ H ₃₂	95
n-Nonylbenzene	Aromatic	15	C ₁₅ H ₂₄	50
n-Hexadecane (cetane)	Paraffin	16	C ₁₆ H ₃₄	100 ^a
2-Methyl-3-cyclohexylnonane	Naphthene	16	C ₁₆ H ₃₄	70
Heptamethylnonane	Paraffin (iso)	16	C ₁₆ H ₃₄	15 ^a
8-Propylpentadecane	Paraffin (iso)	18	C ₁₈ H ₃₈	48
7,8-Diethyltetradecane	Paraffin (iso)	18	C ₁₈ H ₃₈	67
2-Octylnaphthalene	Aromatic	18	C ₁₈ H ₂₄	18
n-Eicosane	Paraffin	20	C ₂₀ H ₄₂	110
9,10-Dimethyloctane	Paraffin (iso)	20	C ₂₀ H ₄₂	59
2-Cyclohexyltetradecane	Naphthene	20	C ₂₀ H ₄₀	57

^aUsed as standards for ASTM D976

octane, blended cetane numbers can differ significantly from those for pure compounds.

Diesel additives. Table 18.20 lists some of the additives used in diesel fuel and the reasons they are used.

Turbine fuel. Kerosene, jet fuel, and turbine fuel have similar boiling ranges. The key product properties are flash point, freezing point, sulfur content, and smoke point. The flash point is the lowest temperature at which a liquid gives off enough vapor to ignite when an ignition source is present. The freezing point is especially important for jet aircraft, which fly at high altitudes where the outside temperature is very low. Sulfur content is a measure of corrosiveness. The measurement of smoke point goes back to the days when the primary use for kerosene was to fuel lamps. To get more light from a kerosene lamp, you could turn a little knob to adjust the wick. But if the flame got too high, it gave off smoke. Even today, per ASTM D1322, smoke point is the maximum height of flame that can be achieved with calibrated wick-fed lamp, using a wick "... of woven solid circular cotton of ordinary quality."

Table 18.20 Diesel fuel additives

Additive type	Function
Anti-oxidation	Minimize oxidation and gum formation during storage
Cetane improvement	Increase cetane number
Dispersion	Improve behavior in fuel injectors
Anti-icing	Minimize ice formation during cold weather
Detergent	Control deposition of carbon in the engine
Metal passivation	Deactivate trace metals that can accelerate oxidation
Corrosion inhibition	Minimize rust throughout the diesel fuel supply chain
Cold-flow improvement	Improve flow characteristics in cold weather

The smoke point of a test fuel is compared to reference blends. A standard 40 %/60 % (volume/volume) mixture of toluene with 2,2,4-trimethylpentane has a smoke point of 14.7, while pure 2,2,4-trimethylpentane has a smoke point of 42.8. Clearly, isoparaffins have better smoke points than aromatics. Table 18.21 lists specifications for common turbine fuels.

Lube base stocks. Refiners prepare lube base stocks from residual oils by removing asphaltenes, aromatics, and waxes. Lube base stocks are hydrofinished, blended with other distillate streams for viscosity adjustment, and compounded with additives to produce finished lubricants. In the past, solvent-based technology was used to prepare lube base stocks. Propane deasphalting was used to remove asphaltenes. Furfural and related substances were used to extract aromatics, and MEK, or MIBK were used to remove wax. With the advent of CDW, some or all of these solvent-based methods can be replaced with hydroprocessing. CDW was developed by Mobil in the 1980s. The process employs ZSM-5, which selectively converts waxy *n*-paraffins into lighter hydrocarbons. The Isodewaxing Process, commercialized in 1993 by Chevron, reduces wax catalytically by isomerising *n*-paraffins into isoparaffins. Isodewaxing also removes sulfur and nitrogen, and it saturates aromatics. Products have a high viscosity index (VI), low pour point, and excellent response to additives.

Waxes. In a traditional lube plant, the raffinate from the solvent extraction unit contains a considerable amount of wax. To recover the wax, the raffinate is mixed with a solvent, usually propane, and cooled in a series of heat exchangers. Further cooling is provided by the evaporation of propane in the chiller and filter feed tanks. The wax forms crystals, which are continuously removed, filtered, and washed with cold solvent. The solvent is recovered by

Table 18.21 Turbine fuel specifications

Specification	Jet A	Jet B	JP-4	JP-5	JP-8
Flash point, °C (min)	38	—	—	60	38
Freeze point, °C (max)	−40 (Jet A) −47 (Jet A-1)	−50	−58	−46	−47
API gravity	37–51	45–57	45–57	36–48	37–51
Distillation, °C					
10 % max	205	—	—	205	205
20 % max	—	145	145	—	—
50 % max	—	190	190	—	—
90 % max	—	245	245	—	—
EP	300	—	270	290	300
Sulfur, wt% max	0.3	0.3	0.4	0.4	0.3
Aromatics, vol% max	22	22	25	25	25
Olefins, vol% max	—	—	5	5	5

flashing and steam stripping. The wax is purified by heating with hot solvent, after which it is re-chilled, re-filtered, and given a final wash.

Making food-grade wax requires wax deoiling with solvents such as methyl-isobutyl ketone (MIBK).

Greases. Greases are made by blending salts of long-chained fatty acids into lubricating oils at 400–600 °F (204–315 °C). Antioxidants are added to provide stability. Some greases are batch-produced, while others are made continuously. The characteristics of a grease depend to a great extent on the counter-ion (calcium, sodium, aluminum, lithium, etc.) in the fatty-acid salt.

Asphalt. Asphalt can be produced directly from vacuum residue or by solvent deasphalting. Vacuum residue is used to make *road-tar asphalt*. To drive off light ends, it is heated to about 750 °F (400 °C) and charged to a column where a vacuum is applied to prevent thermal cracking.

In road-paving, the petroleum residue serves as a binder for aggregate, which can include stone, sand, or gravel. The aggregate comprises about 95 % of the final mixture. Polymers are added to the binder to improve strength and durability. The recommended material for paving highways in the United States is Superpave32 hot-mix asphalt. Superpave was developed in 1987–1993 during a US\$50 million research project sponsored by the Federal Highway Administration.

Roofing asphalt. Roofing asphalt is produced by bubbling air through liquid asphalt at 260 °C (500 °F) for 1–10 h. During this “blowing” process, organic sulfur is converted to H₂S and SO₂. Catalytic salts such as ferric chloride (FeCl₃) may be used to adjust product properties and increase the rates of the blowing reactions, which are exothermic. To provide cooling, water is sprayed into the top of the blowing vessel,

creating a blanket of steam that captures sulfur-containing gases, light hydrocarbons, and other gaseous contaminants. These are recovered downstream. Cooling water may also be sprayed on the outside of the vessel. The length of the blow depends on desired product properties, such as softening temperature and penetration rate. A typical plant blows 4–6 batches of asphalt per 24-h day. There are two primary substrates for roofing asphalt—organic (paper felt) and fiberglass. The production of felt-based roofing shingles consists of:

- Saturating the paper felt with asphalt
- Coating the saturated felt with filled asphalt
- Pressing granules of sand, talc, or mica into the coating
- Cooling with water, drying, cutting and trimming, and packaging

If fiberglass is used as the base instead of paper felt, the saturation step is eliminated.

Insert: the future for petroleum: ethanol in gasoline. In the petroleum industry, few topics are more controversial than ethanol in gasoline. Expert opinions provided during US Congressional hearings confirm the following: For every PhD, there is an equal and opposite PhD. Some facts are indisputable.

- In 2009, the United States and Brazil produced 87.8 % of the world's fuel ethanol, making 10.6 billion gallons and 6.6 billion gallons, respectively [36]
- In the United States, the advantages of putting bio-derived fuels into transportation fuels include cleaner air and less dependence on imported oil. Indeed, replacing 10–15 % of the gasoline in the United States with ethanol would be significant. Most sources say that corn can give 1.1–1.7 times more energy than is required for growing and processing [37]. This energy includes, of course, the production of ethanol. The unfermented “distillers grain” is high in fats and proteins and serves as an excellent animal feed. In contrast, sugar cane gives an energy gain of 8:1
- Thanks to ethanol from sugar cane, Brazil is now energy self-sufficient. Among large Western countries, it is the first to have a sustainable biofuel economy [38]. The eventual production of significant amounts of ethanol from sugar in the United States is unlikely, because it would require substantial investments in infrastructure. In China, the government is investing heavily in obtaining Biofuels from inedible vegetables (not including broccoli). Such fuels include ethanol [39] made from sweet sorghum, sweet potatoes, and cassava

(continued)

- Using corn ethanol for fuel increases food prices, increases consumption of fertilizer and pesticides, and puts pressure on water resources
- Ethanol increases the vapor pressure of gasoline. Therefore, to meet vapor-pressure specifications, refiners must remove butanes and even pentanes from the gasoline blend pool, creating periodic gluts of these compounds in certain areas. The gluts, of course, depress prices for these commodities
- In October 2011, the US government was paying an ethanol subsidy of 45 cents per gallon to oil refining companies and imposing a 54 cents per gallon tariff on imported ethanol. On June 16, 2011 the US Senate voted 73–27 to eliminate the subsidy. The vote did not become law due to White House opposition [40]
- Efficient production of ethanol from cellulose could answer many of the objections to ethanol from corn. Possible substrates are abundant. They include corn stover, switchgrass, miscanthus, and wood chips. The most promising routes involve multistage biological processes such as enzymatic hydrolysis and microbial fermentation. Research in this area is lively [41]

Protecting the Environment

Oil spills. In April 2010, the petroleum industry solidified its reputation for making deadly mistakes that cause titanic damage to the environment. The *Deepwater Horizon* blow-out killed 11 people, injured 17 others, and released up to 4.9 million barrels of oil into the Gulf of Mexico. For additional details, please consult the Report to the President prepared by the National Commission on the BP Deepwater Horizon Oil Spill [42].

Previous oil spills include the following [43]:

On March 16, 1978, the super tanker Amoco Cadiz ran aground on the Portsall Rocks three miles off the coast of Brittany. The wreck broke up completely before any of the remaining oil could be pumped out, so the entire cargo—more than 1.6 million barrels of crude oil—spilled into the sea. The resulting slick was 18 miles wide and 80 miles long. It polluted 200 miles of coastline, including the beaches of 76 Breton communities. The Amoco Cadiz incident caused more loss of marine life than any previous oil spill. Nearly 20,000 dead birds were recovered. About 9,000 tons of oysters died. Fish developed skin ulcerations and tumors. Years later, echinoderms and small crustaceans had disappeared from many areas, but other species had recovered. Evidence of oiled beach sediments can still be seen in sheltered areas, and layers of subsurface oil remain under many impacted beaches.

In March 1989, the super tanker *Exxon Valdez* ran aground in Prince William Sound in Alaska, spilling more than 250,000 barrels of oil into the Sound. Eventually, 33,000 birds and 1,000 otters died because of the spill. To clean up the mess, eleven thousand workers treated 1,200 miles (1,900 km) of shoreline, using 82 aircraft, 1,400 vessels, and 80 miles (128 km) of oil-containing booms. In response to the disaster, the US Congress passed the Oil Pollution Act of 1990. The Act streamlined and strengthened the ability of the U.S. Environmental Protection Agency (EPA) to prevent and react to oil spills. A trust fund, financed by a tax on oil, was established to pay for cleanups when a responsible party cannot afford to do so. The Act requires oil storage facilities and vessels to submit plans that tell how they intend to respond to large oil discharges. EPA published regulations for above-ground storage facilities, and the US Coast Guard published regulations for oil tankers. The Act also requires the development of area contingency plans to prepare for oil spills on a regional scale.

On January 25–27, 1991, during the occupation of Kuwait, Iraqis pumped 4–6 million barrels of oil—16 to 25 times more than the amount spilled by the *Exxon Valdez*—into the Arabian Gulf. On January 27, allied bombers stopped the spill by destroying the pumping stations. Ad Daffi Bay and Abu Ali Island experienced the greatest pollution. Despite the ongoing war, the clean up of the oil spill proceeded rapidly. Kuwaiti crude is rich in light ends, and water in the Arabian Gulf water is relatively warm. For these reasons, about half of the spilled oil evaporated, leaving behind a thick emulsion which eventually solidified and sank to the bottom of the sea. Another 1.5 million barrels were recovered by skimming. But on February 23–27, 1991, retreating Iraqi soldiers damaged three large refineries and blew up 732 Kuwaiti oil wells, starting fires on 650 of them. Up to six million barrels per day were lost between February 23 and November 8, 1991. Crews from 34 countries assembled to fight the oil-well fires. Initially, experts said the fires would rage for several years. But due to the development of innovative fire-fighting technology, the job took less than 8 months.

The oil-well fires burned more than 600 million barrels.

Air quality. In the 1970s and 1980s, environmental laws compelled refineries to reduce emissions of SO_x, NO_x, CO₂, and hydrocarbons. In the atmosphere, SO_x reacts with water vapor to make sulfurous and sulfuric acids, which return to earth as acid rain. Volatile hydrocarbons react with NO_x to make ozone. CO₂ is a major “greenhouse” gas. To reduce these pollutants, the industry tightened its operation by:

- Reducing fugitive hydrocarbon emissions from valves and fittings

- Removing sulfur from refinery streams and finished products
- Adding tail-gas units to sulfur recovery plants
- Reducing the production of NO_x in fired heaters
- Scrubbing SO_x and NO_x from flue gases
- Reducing the production of CO₂ by increasing energy efficiency

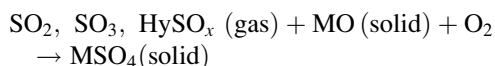
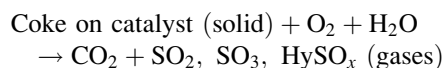
Sulfur recovery. Conversion processes, hydrotreaters, and sweetening units remove chemically bound sulfur from petroleum fractions. The sulfur can end up as SO_x, H₂S, NH₄SH, or NaSH.

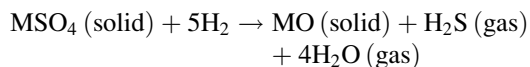
Fuel-oil fired heaters and the regenerators of FCC units are major sources of refinery SO_x and NO_x emissions. The most obvious way to reduce SO_x emissions from a heater is to use low-sulfur fuels. Unfortunately, although that solution requires no investment, it is probably the most expensive due to the relatively high cost of buying low-sulfur fuel oil and/or hydrotreating high-sulfur fuel oil.

A large fraction of the sulfur in the feed to an FCC unit ends up in coke on the catalyst. SO_x are formed in the regenerator when the coke is burned away. Therefore, removing sulfur from the feed, usually by hydrotreating, decreases SO_x emissions. FCC feed pretreating has other substantial benefits. Removing basic nitrogen decreases deactivation of acid sites on the FCC catalyst, which allows the FCC to reach a given conversion at lower temperatures. The saturation of aromatics in the feed pretreater provides the biggest benefit, because it converts hard-to-crack aromatics into easier-to-crack naphthenes. This alone can justify the installation of an FCC feed pretreater.

FCC SO_x transfer additives. SO_x transfer additives, first developed by Davison Chemical, react with SO_x in the FCC regenerator to form sulfates. When the sulfated additive circulates to the riser/reactor section, the sulfate is reduced to H₂S, which is recovered by amine absorption and sent to the sulfur plant. In some units, these additives reduce FCC SO_x emissions by more than 70 %. Consequently, if a pretreater or post-treater still must be installed, its size can be reduced. The chemistry of SO_x transfer is summarized below:

FCC regenerator (oxidizing environment)



FCC Riser-Reactor (reducing Environment)

Flue-gas scrubbing is a refiner's last chance to keep NO_x and SO_x out of the air. In wet flue-gas desulfurization, gas streams containing SO_x react with an aqueous slurry containing calcium hydroxide Ca(OH)₂ and calcium carbonate CaCO₃. Reaction products include calcium sulfite (CaSO₃) and calcium sulfate (CaSO₄), which precipitate from the solution. NO_x removal is more difficult. Wet flue-gas scrubbing removes about 20 % of the NO_x from a typical FCC flue gas. To remove the rest, chemical reducing agents are used. As mentioned above, in the SCR process, anhydrous ammonia is injected into the flue gas as it passes through a bed of catalyst at 500–950 °F (260–510 °C). The chemical reaction between NO_x and ammonia produces N₂ and H₂O.

When sulfur-containing feeds pass through hydrotreaters or conversion units, most of the sulfur is converted into H₂S, which eventually ends up in off-gas streams. Amine absorbers remove the H₂S, leaving only 10–20 wppm in the treated gas streams. H₂S is steam stripped from the amines, which are returned to the absorbers. The H₂S goes to the refinery sulfur plant.

Claus process. At the sulfur plant, H₂S is combined with sour-water stripper off-gas and sent to a Claus unit. Almost every refinery in the world uses some version of this process to convert H₂S into elemental sulfur. H₂S and a carefully controlled amount of air are mixed and sent to a burner, where about 33 % of the H₂S is converted to SO₂ and water. From the burner, the hot gases go to a reaction chamber, where the reactants and products reach equilibrium. In several units, the air is enriched with oxygen to increase plant capacity. Elemental sulfur is produced by the reversible reaction between SO₂ and H₂S. Ammonia comes in with the sour-water stripper off-gas. In the Claus process, it is thermally decomposed into nitrogen and water.

In the Claus burner, combustion temperatures reach 2,200 °F (1,200 °C). Much of the heat is recovered in a waste-heat boiler, which generates steam as it drops the temperature to 700 °F (370 °C). Next, the process gas goes to a condenser, where it is cooled to about 450 °F (232 °C). At this temperature, sulfur vapors condense, and the resulting molten sulfur flows through a drain to a heated sulfur-collection pit. At the bottom of the drain, a seal leg maintains system pressure and keeps unconverted gases out of the pit. Uncondensed sulfur and other gases flow to a series of catalyst beds, which recover additional sulfur by promoting the reaction between leftover H₂S and SO₂. With fresh catalyst and a stoichiometric gas composition, the

cumulative recovery of sulfur across four condensers is about 50 %, 80 %, 95 %, and 96–98 %, respectively.

Tail-gas treating units (TGTU) bring the total sulfur recovery up to >99.9 %. Most tail-gas treating processes send the tail gas to a hydrotreater, which converts all sulfur-containing compounds (SO₂, SO₃, COS, CS₂, and various forms of S_x) into H₂S. In the SCOT process, offered by Shell Global Solutions, the H₂S is absorbed by an amine and returned to the front of the Claus furnace. In the LO-CAT[®] process, offered by Merichem, H₂S is air-oxidized to sulfur in an aqueous solution containing a chelated iron catalyst. For all tail-gas treatment processes, the last traces of unrecovered sulfur go to an incinerator, where they are converted into SO₂ and dispersed into the atmosphere.

Wastewater treatment. Wastewater treatment is used to purify process water, runoff, and sewage. As much as possible, purified wastewater streams are reused in the refinery. Wastewater streams may contain suspended solids, dissolved salts, phenols, ammonia, sulfides, and other compounds. The streams come from just about every process unit, especially those that use wash water, condensate, stripping water, caustic, or neutralization acids.

Primary treatment uses a settling pond to allow most hydrocarbons and suspended solids to separate from the wastewater. The solids drift to the bottom of the pond, hydrocarbons are skimmed off the top, and oily sludge is removed. Difficult oil-in-water emulsions are heated to expedite separation. Acidic wastewater is neutralized with ammonia, lime, or sodium carbonate. Alkaline wastewater is treated with sulfuric acid, hydrochloric acid, carbon dioxide-rich flue gas, or sulfur.

Some suspended solids remain in the water after primary treatment. These are removed by filtration, sedimentation, or air flotation. Flocculation agents may be added to consolidate the solids, making them easier to remove by sedimentation or filtration. Activated sludge is used to digest water-soluble organic compounds, either in aerated or anaerobic lagoons. Steam stripping is used to remove sulfides and/or ammonia, and solvent extraction is used to remove phenols.

Tertiary treatment processes remove specific pollutants, including traces of benzene and other partially soluble hydrocarbons. Tertiary water treatment can include ion exchange, chlorination, ozonation, reverse osmosis, or adsorption onto activated carbon. Compressed oxygen may be used to enhance oxidation. Spraying the water into the air or bubbling air through the water removes remaining traces of volatile chemicals such as phenol and ammonia.

Solid waste handling. Refinery solid wastes may include spent catalyst and catalyst fines, acid sludge from alkylation

units, and miscellaneous oil-contaminated solids. All oil-contaminated solids are treated as hazardous and sent to sanitary landfills. Recently, supercritical extraction with carbon dioxide has been used with great success to remove oil from contaminated dirt.

The Future

Petroleum is one of mankind's primary sources of energy, so anything that affects global energy affects petroleum demand.

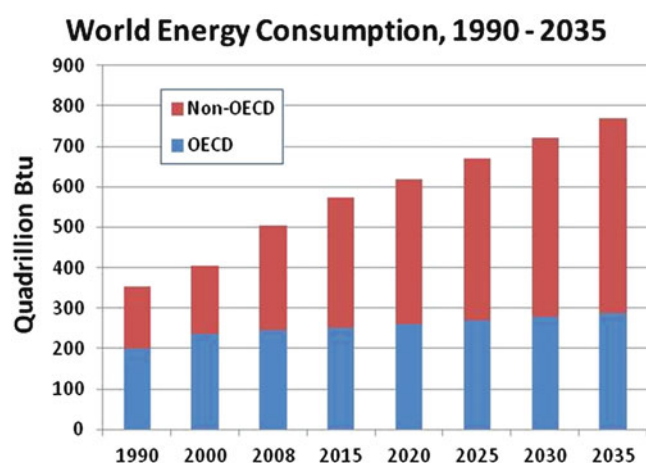


Fig. 18.42 Historical and projected world energy consumption, 1990–2035 [2]

Demand growth in China and India. According to Fig. 18.42, world consumption of energy grew from 350 to 500 quadrillion Btu between 1990 and 2008 and is expected to grow to 780 quadrillion Btu. Non-OECD countries [44], especially China and India, will account for most of the growth. Most likely, on a per capita basis, consumption in OECD countries will still exceed consumption in China and India by wide margin (Fig. 18.43).

Alternatives to petroleum. On average, conventional crude oil is getting harder to find. Over time, unconventional alternatives will supply more and more of our energy and petrochemical monomers. Liquid hydrocarbons will come from natural gas, biomass, bitumen, kerogen, and coal. Some of these contain daunting amounts of contaminants. Even biomass, which includes ethanol and vegetable oils, presents challenges, due the presence of high concentrations of oxygen and olefins. Compared to conventional oil, converting these materials will be costly and more difficult.

EIA's Annual Energy Outlook 2012 [2] projects supplies of unconventional liquids through 2035. The projections were based on three scenarios. In the high-oil-price scenario, future prices will reach \$200 per barrel in 2012. In the reference scenario, which is based on present-day prices, the future price in 2035 reaches \$150. In the low-price scenario, oil reaches \$60 per barrel in 2035. As shown in Fig. 18.45, the largest expected increases come from bitumen and biofuel; biofuel is biomass that has been converted into fuels. In 2009, unconventional liquids supplied about 5 % of world demand. In

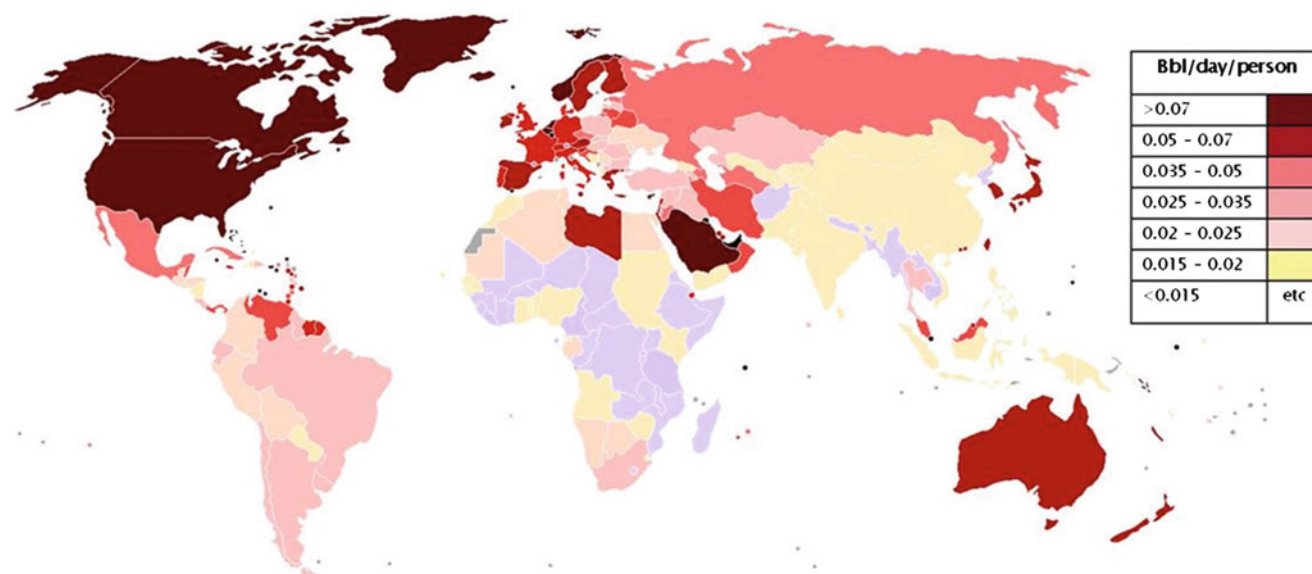


Fig. 18.43 Per capita energy consumption by country, 2009 [45]

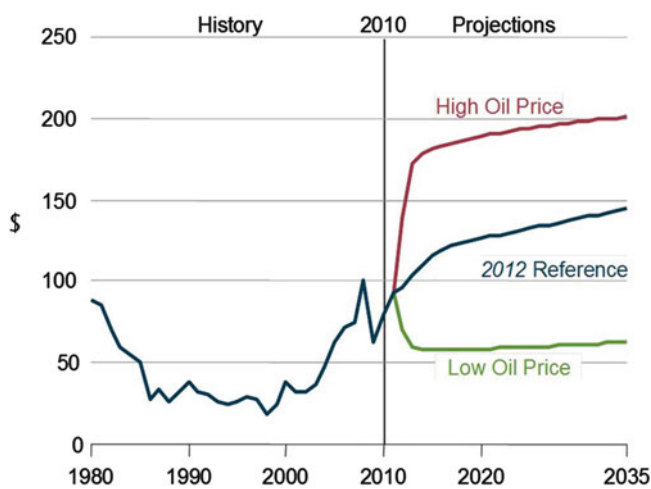


Fig. 18.44 Basis for the EIA forecast on the future use of unconventional liquids as replacements for conventional petroleum

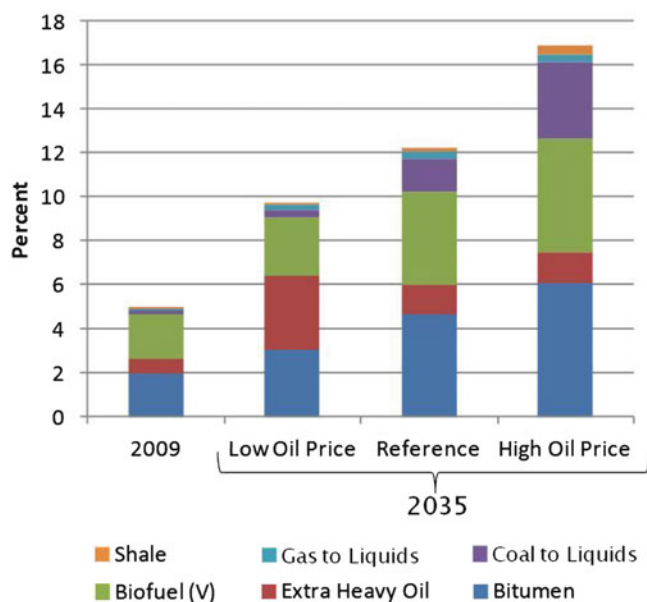


Fig. 18.45 Projected sources of unconventional hydrocarbon liquids in 2035, as a function of the scenarios shown in Fig. 18.44

EIA's high-oil-price scenario, by 2035 they will account for nearly 17 %. In the low-price scenario, by 2035 they will supply less than 10 %. The percentage of unconventional liquids will be higher at high oil prices, because the relative production cost (compared to conventional crude) will be lower.

Ethanol and other biofuels. Many countries now require the blending of ethanol or other oxygen-containing chemicals into gasoline. The oxygen content of fossil hydrocarbons is low. So is the oxygen content of most

petrochemical monomers. In contrast, ethanol, cellulose, and vegetable oil contain a lot of oxygen, which must be removed before they can replace petroleum or natural gas in existing petrochemical plants. Removing oxygen is expensive and inefficient. Given enough time, we could develop a new bio-based chemical industry [46]. But in meantime, if we would decrease the amount of petroleum we burn, we would extend the time we could use it for polymers and plastics.

Adding 10 % ethanol to gasoline decreases the demand for petroleum, not by 10 %, but to some extent. This is because the production of ethanol requires energy. As mentioned, the estimated energy gain for ethanol from corn ranges from 1.1 to 1.7, while the energy gain for ethanol from sugar is 8:1 [36–38].

Automation. The ever-increasing development and use of better instruments and analyzers, engineering models, and real-time online optimization continue to improve the efficiency and safety of petroleum processing plants. In one case [47], implementing advanced process control increased production by 2.5 % at the Chemopetrol ethylene plant in Litvinov, Czech Republic. Other examples are provided on the web sites of companies such as Applied Manufacturing Technologies, Aspen Technology, Emerson Process Management, Honeywell Process Solutions, Invensys Operations Management, Yokogawa, and others.

Hampton and Robinson [48] provide an example of the use of advanced regulatory control to improve the safety of hydrocracking units.

Protection of the environment. The push to control anthropogenic CO₂ emissions is gaining momentum (see the inset for additional comments). Government agencies around the world continue to tighten regulations on sulfur in fuels, air quality, wastewater quality, and the disposal of hazardous solids. Such regulations are now being adopted in less developed countries. They improve the quality of air, water, and land, but they also require investment.

Conservation. Conservation also decreases the demand for petroleum. As mentioned above, with modest investment in proven, widely applied technology, the United States could increase the efficiency of power production by 30 % [4]. Prices have a tremendous effect on energy conservation, which can be accomplished by turning off lights and driving less, but also due to innovation.

Encouraging energy conservation is an obvious, low-cost, win-win way to reduce CO₂ generation on a very large scale [4]. Other solutions, such as replacing coal-bed methane with CO₂, are technically sound, but their potential impact is minor. However, the sum of several minor solutions can be quite significant.

At present, it looks like the world is moving toward punitive measures, such as carbon taxes and/or cap-and-trade. The impact of these could be limited, because businesses with high emissions can avoid investing in energy efficiency by purchasing carbon credits [49].

Never underestimate the ingenuity of a hungry human.

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